Research Article

Natural Background Concentrations Determination for Metals in Surface Waters, Gediz River Basin

Yüzey Sularındaki Metaller için Doğal Arka Plan Konsantrasyonlarının Belirlenmesi, Gediz Havzası Örneği

Betul Hande Gursoy-Haksevenler^{1,} , Elif Atasoy-Aytış², Mehmet Dilaver², Elif Küçük³, Tolga Pilevneli³, Ülkü Yetiş³, Aybala Koç Orhon⁴, Esra Şıltu⁴

¹Marmara University, Faculty of Political Science, Department of Political Science and Public Administration, Urbanization and Environmental Problems Program, 34820, Beykoz, İstanbul hande.gursoy@marmara.edu.tr

²TUBITAK Marmara Research Center (MRC), Environment and Cleaner Production Institute, 41470, Gebze, Kocaeli

elif.atasoy@tubitak.gov.tr, mehmet.dilaver@tubitak.gov.tr

³Middle East Technical University, Department of Environmental Engineering, 06800, Çankaya, Ankara ekucuk@metu.edu.tr, ptolga@metu.edu.tr, uyetis@metu.edu.tr

⁴Republic of Turkey Ministry of Agriculture and Forestry, General Directorate of Water Management, 06510, Yenimahalle-Ankara

aybala.kocorhon@tarimorman.gov.tr, esra.siltu@tarimorman.gov.tr Received Date: 17.11.2017, Accepted Date: 05.04.2018

Abstract

In this study, an approach was developed for natural background concentration determination of metals and metalloids (Ag, Al, As, B, Co, Cr, Cu, Fe, Sb, Sn, V, Zn, Ti, Cd, Ni, Pb and Hg) listed in By-law on Surface Water Quality (OG: 30.11.2012/28483) as priority substances or specific pollutants. Gediz River Basin was selected as a pilot area and seasonal monitoring studies were conducted in the selected surface waters during 2015-2016. For determination of NBC, it is necessary to distinguish whether the presence of metals detected in the receiving environment is natural or anthropogenic. In this context, anthropogenic sources were monitored and evaluated according to the pollution contribution of each pressure; natural sources of investigated metals were considered according to mining activities and geothermal source distribution. A methodology was developed and applied by indicating the relative contribution of pollutant resources and whether critic value was exceeded or not. Pollution contribution was calculated representing the relative effect of anthropogenic sources. This approach was found suitable for determining NBC and could be helpful for decision makers by establishing critical factors (e.g. which facility should be established where; which plant can discharge its pollutant in which amount; what kind of precautions should be taken in agricultural activities; as well as how to reduce the pesticides used) while comparing the effect of pollution sources.

Keywords: Metals, surface waters, water quality, natural background concentration, environmental quality standards

Öz

Bu çalışmada, Yerüstü Su Kalitesi Yönetmeliği'nde (RG: 30.11.2012/28483) yer alan öncelikli maddeler ve Pb ve Hg için doğal arka plankonsantrasyonlarının belirlenmesine yönelik bir yaklaşım geliştirilmiştir. Bu amaçla Gediz Nehir Havzası pilot havza olarak seçilmiş ve belirlenen yüzey suları 2015-2016 yılları arasında mevsimsel olarak izlenmiştir. Doğal arka plan konsantrasyonlarının belirlenmesi için, alıcı ortamda tespit edilen metallerin varlığının, doğal kaynaklı mı yoksa antropojenik kaynaklı mı olduğunu ayırt etmek gerekmektedir. Bu kapsamda, antropojenik kaynaklar için olası her baskının kirlilik katkısı

izleme çalışmaları yapılarak incelenmiş; doğal kaynaklar için madencilik faaliyetleri ve jeotermal kaynakların dağılımı değerlendirilmiştir. Antropojenik kaynakların kirletici etkisinin tespit edilmesi ve buna bağlı olarak Doğal arka plan konsantrasyonlarının belirlenmesi için kirlilik katkı yüzdesinin hesaplandığı bir metodoloji ortaya konmuştur. Geliştirilen bu yaklaşımla, yüzey sularında doğal arka plan konsantrasyonları belirlenebilmekte ve kirlilik kaynaklarının alıcı ortam üzerindeki etkisi ayırt edilebilmektedir. Buna bağlı olarak, geliştirilen yaklaşımın, karar vericilerin kritik kararları (hangi tesisin nerede kurulması gerektiği, hangi tesisin ne oranda kirletici deşarj edebileceği, tarımsal üretimde ne gibi önlemlerin alınması gerektiği, kullanılan zirai mücadele ilaçlarının ne oranda azaltılmasının uygun olacağı gibi) almasına yardımcı olacağı düşünülmektedir.

Anahtar kelimeler: Metaller, yüzey suları, su kalitesi, doğal arka plan konsantrasyonu, çevre kalite standardı

Introduction

Natural background concentration (NBC) is defined as the concentration of a chemical substance originating from natural and geological processes (EC, 2011). It is identified by the presence of chemical substances in the receiving water body as a result of natural processes joining the water either through point and diffuse sources. Determination of NBC of a pollutant in the water body has great importance while determining the Environmental Quality Standard (EQS) for that specific pollutant in order to define 'good ecological and chemical status' and to improve the water quality. NBC of pollutants in the water bodies varies according to typology, geology, geography of the watershed and to physical, chemical and biological features of the groundwater.

In the European Water Framework Directive (WFD; 2000/60/EC) (EC, 2000), the environmental objective is to achieve good surface water status in all Member States. For this purpose, environmental quality standards have been issued, either by the European Commission for priority substances, or by the Member States for river basin specific pollutants. In case of non-compliance with the standard, Member States are allowed to take account of NBCs or bioavailability. Thus, determination of NBC for relevant substances (e.g. trace metals) is required. WFD allows a correction for NBC only for metals though some organic contaminants also have a natural origin. WFD does not necessitate the derivation of NBC; therefore, each country can derive their own NBC.

In Turkey, Turkish By-law on Surface Water Quality (OG:30.11.2012/28483) covers metal and metalloid parameters of Ag, Al, As, B, Co, Cr, Cu, Fe, Sb, Sn, V, Zn, Ti, Cd, Ni, Pb and Hg either as priority substances listed in Table 5 or specific pollutants listed in Table 4 of Annex 5 for determination of NBC.

Several methods have been proposed to derive NBC of trace metals for surface waters such as i) the clean streams approach (based on measurements in relatively undisturbed aquatic systems); ii) the sediment approach (based on the composition of sediments and equilibrium partitioning); iii) the spring of surface water (based on natural background level based on groundwater background concentrations); iv) monitoring data approach, and v) stable summer levels as ambient background concentration (Oste et al., 2011). For instance, NBC for Dutch surface waters are derived according to the clean streams approach for As, Ba, Be, Cd, Cr, Co, Cu, Pb, Hg, methyl-Hg, Mo, Ni, Se, Ti, Sn, V, and Zn and published in the Dutch 4th National Water Plan (1998). In UK, monitoring data approach was applied for derivation of ambient NBCs of metals (Peters et al., 2010).

In this study, 40 monitoring stations on surface waters were seasonally (4 periods) monitored during 2015-2016. Simultaneously, municipal discharges (29 points) and industrial discharges (54 points) sources were also monitored to determine the effect of point sources on the ambient water quality. For determination of NBC, a novel approach was developed since the inadaptability of existing data to present NBC determination methods used by other countries. Before developing a new approach, the suitability of present methods was investigated. Among the referred methods, "clean streams approach" and "monitoring data approach" seemed more appropriate for NBC determination. However it was recognized that these methodologies were not suitable when considering the available data. Clean streams approach, developed and described by Zuurdeeg et al. (1992) and used in the Netherlands, is based on the principle of water quality of the upstream waters in relatively unpolluted regions. However in this study, only one point among the receiving body monitoring points could be characterized as an upstream point although it was not a representative point for the entire basin. In monitoring data approach, based on a document of the Environment Agency and used in the UK, there should ideally be a minimum of 5 continuous monitoring data on at least 50 stations for derivation of NBC (Peters et al., 2010). But in this study, obtained monitoring data was not sufficient to apply the aforementioned methods. Therefore, instead of using pre-referred approaches, a new methodology was developed to calculate NBC values by taking into account the natural and anthropogenic sources affecting the surface water bodies. Relatively unpolluted monitoring points were selected and the pressures affecting the water quality at these points were investigated. Pollution caused by each pressure on the corresponding receiving water was evaluated by using its contribution ratio regarding pollution load. If the receiving body was identified as highly polluted due to a point source, the monitoring point at this receiving body was not taken into consideration for the assessment of NBC, and the rest of the monitoring stations were evaluated by considering their proximity to the existing geologic formation and mining sites

Although several studies have been proposed for the determination of metal contamination in surface waters, sediments and biota samples in Gediz River Basin (Bizsel et al., 2017; Suzer et al., 2015; Aydin and Kucuksezgin, 2012; Kucuksezgin et al., 2008), these studies were subjecting the presence of metals and investigating the source metal pollution. However for NBC determination, there is still a lack of studies for both Gediz River Basin and Turkey. This study aims to develop a methodology for determining NBC for metals in surface waters. In that sense, it might be considered as a pioneer study for presenting an approach for NBC determination in Turkey. A method was set considering both natural and anthropogenic effects on water quality. For natural effects, mining areas and geothermal wells were taken into consideration while municipal and industrial wastewater discharges and solid waste dumping sites were evaluated for assessing the anthropogenic effect.

Method

Study Area

Gediz River Basin covers the region between Northern Aegean, Susurluk and Kucuk Menderes River Basins, located in the western part of Turkey discharging its waters via Gediz and its branches to Aegean Sea that is an elongated bay of Mediterranean Sea. The basin area is 1,703,394 ha and it covers 2.17% of Turkey. Gediz River has a length of 275 km, and its yearly average water potential is calculated as 2,270 hm³ or 126 mm. Four sub-basins are determined by considering hydrologic and topographic conditions of the basin (MoFWA, 2015). The sub-basins are listed from upstream to downstream as i) Upper Gediz, ii) Alasehir Stream, iii) Gordes-Gurduk Stream and iv) Lower Gediz. The map demonstrating the sub-basins is provided in Figure 1.

Gediz River Basin has a great importance due to intensive industrial and agricultural activities. Textile, food, leather, food processing, construction materials, dairy, meat and poultry processing and manufacturing of agricultural vehicles are the predominant industries in the basin (MoFWA, 2017). Especially the sub-basins of Lower Gediz and Nif Stream are the main industrialized regions. In terms of agricultural activities, 50% of the basin area is used for the cultivation of different agricultural products mainly includes grape, cherry, olive, tomato, walnut and cotton (MoFWA, 2017, MoFAL, 2016).

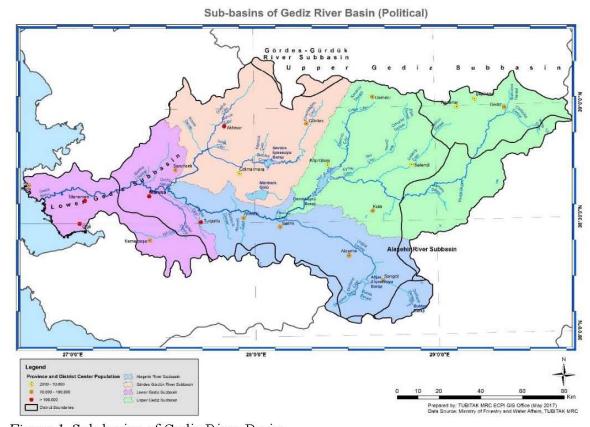


Figure 1. Sub-basins of Gediz River Basin.

Monitoring Program

Within the scope of this study, 40 stations in the mainstream and tributaries of Gediz River were seasonally monitored during the periods of 01-18 November 2015 (autumn), 01-17 February 2016 (winter), 02-17 May 2016 (spring) and 01-19 August 2016 (summer). Surface water monitoring programs were determined by taking into consideration i) the previous points of a discharges such as industrial facilities, urban discharges and urban wastewater treatment plants' (WWTPs), ii) if there was a new branch combining with main stream, both a point on this new branch and another point after their combination were chosen, iii) if there was a dam, points on branches both entering and leaving the dam were chosen, iv) if there was a possibility for reaching relatively clean conditions, points such as origins of streams were selected. Monitoring stations are presented in Figure 2. Metal parameters of Ag, Al, As, B, Co, Cr, Cu, Fe, Sb, Sn, V, Zn, Ti, Cd, Ni, Pb and Hg, which are among the priority substances in Table 5 and point specific pollutants in Table 4 of Annex 5 in By-law on Surface Water Quality (OG:30.11.2012/28483), are studied for determining NBC.

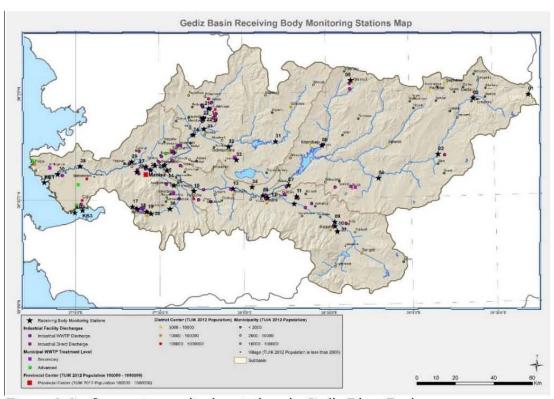


Figure 2. Surface water monitoring stations in Gediz River Basin.

Table 1
Instrumental Analyses Used in the Present Study

				Detection Limit	Quantification	
Parameter CAS No		Analysis	Instrument	(LOD) (μg/L)	Limit (LOQ) (μg/L)	
Hg	7439-97-6	TS 2537 EN 1483:1999-4	AAS Cold Steam	0.04	0.13	
Pb	7439-92-1	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.022	0.066	
Ni	7440-02-0	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.021	0.073	
Cd	7440-43-9	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS , 81VN3092001	0.019	0.059	
Al	7429-90-5	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.197	0.512	
Sb	7440-36-0	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.042	0.12	
As	7440-38-2	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.067	0.209	
Cu	7440-50-8	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.091	0.263	
В	7440-42-8	ISO 11885 ICP-OES	NEXION 300XX model ICP-MS, 81VN3092002	0.025	0.067	
Zn	7440-66-6	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS , 81VN3092001	0.142	0.667	
Fe	7439-89-6	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.839	2.172	
Ag	7440-22-4	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.007	0.021	
Sn	7440-31-5	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	3	10	
Со	7440-48-4	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.008	0.026	
Cr	7440-47-3	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 1VN3092001	0.065	0.2	
Ti	7440-32-6	ISO 11885 ICP-OES/SM 4500-SiO2-:2005 F Colorimetric Method	PERKIN ELMER 8300 ICP- OES/Scalar autoanalyzer	2.3	7.67	
V	7440-62-2	EPA 6020 A ICP-MS	NEXION 300XX model ICP-MS, 81VN3092001	0.008	0.021	

Assessment of NBC

EQS values are limit values for protection of environment and human health from substances reached to the ambient by man-made activities. EQS are determined according to the ecotoxicology data of the related chemicals. While determining the EQS values for substances such as trace metals, defining of NBC that is the concentration originates from natural and geological processes is significant.

While determining the effect of anthropogenic pressure on the receiving water body, pollution contribution was calculated according to the equations (Equation 1 and

2) given below. If the calculated increase is higher than 2%, it is accepted that the related receiving body is under anthropogenic pressure (EC, 2008; EC, 2010).

$$\frac{PC}{EQS}x100 = \% increase$$

Equation 1

where;

PC = Process Contribution EQS = Environmental Quality Standards

$$\frac{\left[CoC\right]_{\mathit{eff}} x Q_{\mathit{eff}}}{\left(Q_{\mathit{river}} + Q_{\mathit{eff}}\right)} = PC$$

Equation 2

where;

CoC = Metal concentration in wastewater $Q_{eff} = Wastewater$ flow rate $Q_{river} = River$ flow rate

For the pressures with at least 2% pollution contribution, geological formations around the region were investigated. If there appears a geological formation around the water resource that has the potential of metal concentration, the monitoring station was included in NBC calculation; if not, the pressure was considered to be anthropogenic and the associated monitoring station was excluded. For each metal, NBC was calculated by taking the mean value of the seasonal monitoring data. NBCs were calculated for 17 metal parameters.

Following the derivation of the NBCs the final EQSs of the metals in Gediz River Basin were also determined by using the approach specified below.

• If NBC is lower than EQS, Environmental Objective (EO) is equal to EQS.

$$NBC < EQS \rightarrow EO = EQS$$
(3)

• If NBC is equal to or higher than EQS, EO is equal to the sum of EQS and NBC.

$$NBC \ge EQS \to EO = EQS + NBC \tag{4}$$

The aquatic environment can be affected by chemical pollution both in the short and long term, which is defined by acute and chronic effects, respectively. For providing protection against long-term exposure, EQS expressed as an annual average (AA-EQS) value, on the other hand, for providing protection against short-term exposure, maximum allowable concentrations (MAC-EQS) is used (EC,2011).

Considering the distribution of anthropogenic pressures, stations located in the Lower Gediz Sub-basin (downstream of Gediz River that reaches to Aegean Sea) and Nif Stream Sub-basin were eliminated because of under pressure of municipal and industrial discharges and being far away for determining the naturally presence of metals. For this reason 27 stations out of 40 stations were investigated for NBC assessment. For these 27 stations, the pressures were identified and their contribution to metal pollution in the surrounding receiving bodies was calculated.

Results & Discussion

Mean values of the seasonal monitoring data are presented in Table 2. Most of the metal concentrations were found to be higher than their AA-EQS with the exception of Ag, As, Ba, Be, Sb and Sn. The colored fields in the table were represented the exceeded AA-EQS values. Furthermore, it was found that the metal concentrations were higher in the downstream (Lower Gediz Sub-basin) compared to the upstream (Upper Gediz Sub-basin). Depending on higher values mostly being the result of anthropogenic pressures, stations taken place in in the Lower Gediz and Nif Stream Sub-basins were not evaluated for NBC determination.

In order to determine NBC values, it is significant to identify the presence of metals as a result of natural processes. Among the stations, there is only TMDL-01 station located in the source of the basin that is far away from anthropogenic pressures. According to the ecological monitoring results obtained by the project of Sensitive Areas and Determination of Water Quality Objectives, TMDL-01 station was defined as suitable for being a reference point for Gediz Basin (MoFWA, 2015). However, the typology of the water body in which TMDL-01 is located does not represent the entire basin. Therefore, the result of determining the NBC value on a single station is not found appropriate. Afterwards for aiming to evaluate the characteristic of entire basin, the monitoring results of 40 stations were considered for NBC by screening extreme values. However, at this stage it was a question mark that the effect of anthropogenic pressures could not be eliminated. At the final point, it was decided not to take stations on Lower Gediz Lower Sub-basin (downstream of Gediz River that reaches to Aegean Sea and Nif Stream), where anthropogenic pressures were intense, and the remaining 27 stations were examined for NBC determination.

Table 2
Monitoring Data of Metals in Surface Waters (Annul Values)

AA-EQS Values (particular) TMD	DL_01 0.0 DL_02 0.1 DL_03 0.1 DL_04 0.3 DL_05 0.1 DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	2.2 5 110 6 342 4 576 2 61 2 406 2 1.5 103 5 189	As 53 1.3 9 42 63 70 57 16 28	B 707 55 211 562 508 225 1223 341 443	Cd 0.08 0.10 0.09 0.11 1.26 0.13 0.15 0.16	Co 0.3 0.51 1.33 1.57 38 0.27 1.31	Cr 1.6 9 11 9 145 1.1	Cu 1.6 17 13 18 71	Metals (μg/l Fe 36 276 809 1169	Ni 4 12 27 28	Pb 1.2 1.63 1.83 3	7.8 0.70 1.45 1.39	Sn 13 <10 <10 <10	V 1.6 0.44 1.54 2.5	5.9 40 27 41	Hg 0.07 < 0.13 < 0.13 < 0.13	Ti 26 < 7.67 < 7.67
Upper Gediz TMD	DL_01 0.0 DL_02 0.1 DL_03 0.1 DL_04 0.3 DL_05 0.1 DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	5 110 342 4 576 2 61 406 2 1.5 103 189	1.3 9 42 63 70 57 16 28	55 211 562 508 225 1223 341	0.10 0.09 0.11 1.26 0.13 0.15	0.51 1.33 1.57 38 0.27	9 11 9 145 1.1	17 13 18 71	276 809 1169	12 27	1.63 1.83	0.70 1.45	< 10 < 10	0.44 1.54	40 27	< 0.13 < 0.13	< 7.67 < 7.67
Upper Gediz Upper Gediz TMD TMD TMD TMD TMD TMD TMD TM	DL_02 0.1 DL_03 0.1 DL_04 0.3 DL_05 0.1 DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	342 576 2 61 2 406 1.5 2 103 5 189	9 42 63 70 57 16 28	211 562 508 225 1223 341	0.09 0.11 1.26 0.13 0.15	1.33 1.57 38 0.27	11 9 145 1.1	13 18 71	809 1169	27	1.83	1.45	< 10	1.54	27	< 0.13	< 7.67
Upper Gediz TMD TMD TMD TMD TMD TMD TMD TMD TMD TM	DL_03 0.1 DL_04 0.3 DL_05 0.1 DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	576 2 61 2 406 2 1.5 2 103 5 189	42 63 70 57 16 28	562 508 225 1223 341	0.11 1.26 0.13 0.15	1.57 38 0.27	9 145 1.1	18 71	1169								
Upper Gediz TMD	DL_04 0.3 DL_05 0.1 DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	61 406 2 1.5 2 103 5 189	63 70 57 16 28	508 225 1223 341	1.26 0.13 0.15	38 0.27	145 1.1	71		28	3	1.39	< 10	2.5	41	< 0.13	1.0
TMD	DL_05 0.1 DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	2 406 2 1.5 2 103 5 189	70 57 16 28	225 1223 341	0.13 0.15	0.27	1.1		= <000								13
TMD TMD TMD TMD TMD TMD TMD TMD	DL_06 0.2 DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	1.5 103 189	57 16 28	1223 341	0.15				76888	249	27	3	< 10	114	187	2.8	2132
TMD TMD TMD TMD TMD TMD TMD	DL_07 0.1 DL_08 0.1 DL_09* DL_10 0.2 DL_11*	103 189	16 28	341		1.31		14	496	2.3	2	1.07	< 10	1.5	30	0.17	< 7.67
TMD TMD TMD TMD TMD	DL_08 0.1 DL_09* DL_10 0.2 DL_11*	189	28		0.16		4.4	13	2035	5.2	2.6	1,3		6	26	0.14	141
TMD TMD TMD	DL_09* DL_10 0.2 DL_11*		3.0010	443		0.24	1.3	13	239	5.2	1.5	1.2	< 10	4.5	58	0.19	< 7.67
TMD TMD	DL_10 0.2 DL_11*	14	MI MONTH		0.09	0.32	1.03	14	331	4.5	1.2	1.1	< 10	2.6	29	0.18	< 7.67
TMD	DL_11*	14	Table to see														
			82	1642	0.66	16	64	54	23180	54	19	6	< 10	49	188	0.73	597
TIVID	DL 37 0.1	1.1	21	167	0.16	1.4	3	17	2025	6	2.5	2.7	< 10	4.7	49	0.30	186
	$DL_{40} = 0.1$	380	36	10652	0.08	1.8	1.7	13	1372	3.9	1.6	12		3	38	0.49	18
	$DL_{12} = 0.1$	5 1.2	37	4537	0.09	2.5	5	15	3217	6	2.2	1.4	< 10	6	161	0.17	76
TMD	$DL^{-}13$ 0.1	5	80	1932	0.29	4	58	22	6667	14	5	4.5	< 10	14	89	< 0.13	356
TMD	DL 14 0.0	3 1.1	48	1213	0.2	1.3	5	12	1975	6	3	1.4	< 10	5	35	< 0.13	26
TMD	$DL^{-}15$ 0.0	323	38	384	1.62	0.54	2	16	794	4	3	0.72	< 10	2	60	0.30	< 7.67
TMD	DL 21 0.0	3 1.3	2.7	63	0.65	2.4	11	16	1807	26	3	0.18		6	185	0.31	31
	DL 22 1 0.3		27	141	1.13	30	137	71	33268	260	19	0.48		61	105	0.31	772
	DL 22 2 0.1		10	580	0.34	4.1	14	33	2488	25	9	1.08	< 10	12	165	0.41	80
	DL 23 0.1	74	5	186	0.10	0.5	4	12	194	4	2	0.28		1.23	34	0.23	< 7.67
	DL 24 0.1		24	255	0.17	7	27	28	8193	38	9	1.02	< 10	20	104	0.50	736
	DL 25 0.0	320	21	197	0.13	1.1	4	17	618	8	2	1.27	< 10	6	35	0.32	< 7,67
TMD	DL 31 0.1		15	57	0.21	1.3	5	16	2239	6	3	0.50	< 10	8	48	0.37	251
	$DL_{32} = 0.2$	2 7	23	109	1.85	5	23	28	9022	28	8	0.66		23	54	0.46	354
	DL 33 0.1	8	33	168	0.23	6	25	29	9381	33	8	0.92	< 10	23	65	0.76	1260
	DL^{-34} 0.1		35	327	0.1	0.23	1.07	17	304	5	2.6	1.22	< 10	3	43	0.40	< 7.67
TMD	DL 16 0.0	518	35	584	0.36	1	3.9	15	1068	6	3	0.77	< 10	3	66	0.27	< 7.67
	$DL^{-}17$ 0.0		9	67	0.27	0.3	1.2	10	330	2	2	0.24	< 10	2	70	0.07	< 7.67
Nif Stream TMD	$DL^{-}18$ 1.0	1172	11	993	0.85	2.5	1046	380	2004	2969	97	1.98	< 10	5	1416	0.25	< 7.67
	DL 19 0.9	7 7505	10	691	3.5	19	50	56	3103	79	44	1.86	15	7	4145	0.47	44
	DL 39 0.4	2366	7	469	0.2	9	77	56	1034	228	17	2.7	< 10	4	15725	0.41	< 7.67
	DL_36 0.1	405	7	228	0.13	1.7	24	24	631	59	4	0.89	< 10	2	175	0.38	< 7.67
	$DL_{20} = 0.1$	44965	104	272	0.32	16	80	46	50571	81	26	1.78	< 10	65	402	0.38	889
TMD	DL 26 0.0	1303	47	1070	0.22	1.5	6	13	2280	8	3	1.58	< 10	6	40	0.32	68
	$DL^{-}27$ 0.1	2889	46	794	0.21	3.6	12	20	5107	21	6	1.34	< 10	10	81	0.39	54,25
Lower Gediz TMD	DL 28 0.0	633	4	376	0.81	0.8	11	712	2220	21	6	0.77	< 10	3	154	0.75	< 7.67
	DL ²⁹ 0.0		45	785	0.7	3.6	21	27	6486	31	6	1.42	< 10	9	87	0.50	69
	DL ³⁸ 0.0	2653	45	679	0.24	3.7	26	25	4208	36	12	1.20	< 10	10	101	0.33	67
	DL 30 0.0		40	708	0.94	1.6	8	14	1470	20	3	1.36	< 10	7	174	0.50	12

Note. These stations were observed as dry during monitoring. As a consequence, no data is available.

For comparing the obtained results (during 2015-2016), the monitoring studies conducted by the State Hydraulic Works (DSI) which were more representing for long term (during 2000-2015) were analyzed (DSI, 2016). However, it was determined that all metals listed in By-law on Surface Water Quality (OG: 30.11.2012/28483) were not being monitored. Besides the monitored parameters were not frequent for giving an idea. In addition to DSI, the Ministry of Environment and Urbanization also had monitoring studies for surface waters, but these observations were less comprehensive and less detailed when compared with the current study. Nevertheless similar results were obtained for the common parameters monitored.

The locations of the point source pressures are shown in Figure 3. The mining areas (mines in operation, mines not currently in operation, and mine potential) and geothermal wells are presented in Figure 4 to provide insight about geological formation of the basin.

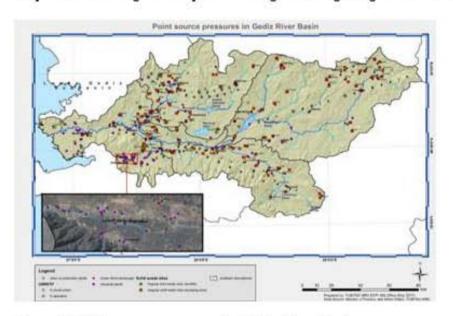


Figure 3. Point source pressures in Gediz River Basin.

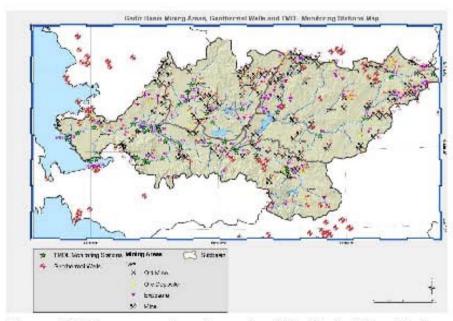


Figure 4. Mining areas and geothermal wells in Gediz River Basin.

The pressures affecting the water quality on each station were assessed considering their pollution contribution. Discussion on the NBC value was made for each metal in following sections.

Ag

It was observed that AA-EQS value of 1.5 μ g/L for Ag was not exceeded in any stations. Relatively high Ag concentrations were obtained only in the stations of TMDL-18, TMDL-19 and TMDL-39 located around Nif Stream. None of the pressures detected in the basin exceeded a pollution contribution of 2% in the receiving water bodies. Accordingly, NBC value calculated for Ag was found as lower than the EQS value.

Al

Al concentrations have been observed as higher than the AA-EQS value of 2.2 μ g/L for all the stations. The obtained values have ranged from 74 μ g/L (TMDL-23) to 61147 μ g/L (TMDL-04). There are kaolin deposits in the Upper Gediz Sub-Basin (around TMDL-01, TMDL-02, TMDL-03), kaolin potentials around the upstream of Alasehir Stream Sub-Basin and kaolin operations around the stations of TMDL-09, TMDL-10 and TMDL-37. In addition, zeolite and feldspar operations are present around TMDL-06 in the vicinity of Demirci and near the TMDL-31 station located in Gordes-Gurduk Stream Sub-Basin. Apart from these regions, receiving water bodies affected by anthropogenic pressures by at least 2% were excluded from NBC evaluation. On the other hand, in rainy period, relatively high Al concentrations were observed at some stations, which are associated with existing geological formations.

As

As was detected over 50 μ g/L in the stations located around Demirci (TMDL-05, 70 μ g/L), Koprubasi (TMDL-06, 57 μ g/L), Kula (TMDL-04, 63 μ g/L), Ahmetli (TMDL-13, 80 μ g/L), Alasehir (TMDL-10, 82 μ g/L) and Nif Stream mouth (TMDL-20, 104 μ g/L). Similar results were obtained also in groundwater monitoring studies conducted by the State Hydraulic Works (DSI). In groundwater monitoring, it was observed that As value increased depending on the geological structures in various regions of the basin. As concentrations were observed over 100 μ g/L in groundwater around Demirci, near Gure, around Borlu and Salihli, in the east of Manisa provincial center and in Menemen and its surroundings (DSI, 2016). As concentration measured in groundwater during dry period was identified as higher compared to the concentration in rainy periods. The high arsenic concentration in the study has been largely associated with the geological structure.

В

Boron concentrations detected in the stations of TMDL-40 (10652 $\mu g/L)$, TMDL-10 (1642 $\mu g/L)$, TMDL-12 (4532 $\mu g/L)$, TMDL-13 (1932 $\mu g/L)$ and TMDL-14 (1213 $\mu g/L)$ located in Alasehir Stream Sub-basin were relatively higher compared to other stations. It has been observed that geothermal wells were located in this region. Therefore, it is possible to state that the B detected is of natural origin.

Co

The concentrations of Co measured in the majority of the receiving water stations were found to be higher than 0.3 μ g/L, which is the AA-EQS value. The higher concentrations were observed at TMDL-04 (38 μ g/L), TMDL-10 (16 μ g/L), and TMDL-22-1 (30 μ g/L). When the concentration values were converted to load unit, it has been observed that higher Co loads were introduced around Akhisar and Manisa-Center. Co is not found as a mineral naturally occurring in the basin. In receiving water bodies where Co was determined to be relatively high, the pressures at least with a 2% pollution contribution were identified. The contamination in these waters was assumed to be of anthropogenic origin and the stations were not taken into consideration for NBC evaluation.

\mathbf{Cr}

AA-EQS value of Cr parameter, which is equal to 1.6 μ g/L, was mostly exceeded in the monitoring stations. The higher values were obtained in TMDL-04 with a value of 145 μ g/L and in TMDL-22-1 with 137 μ g/L. There are no chromium deposits in the basin. It was observed that there were pressures with at least 2% contribution in the receiving bodies in which Cr concentrations were determined as relatively higher. It was accepted that the pollution in aforementioned receiving bodies was of anthropogenic origin, thus these receiving bodies were not taken into consideration for NBC evaluation.

Cu

Cu concentration measured in majority of the stations was found higher than 1.6 μ g/L, which is AA-EQS value. Higher values were observed in the stations of TMDL-04 (71 μ g/L), TMDL-10 (54 μ g/L) and TMDL-22-1 (71 μ g/L). There are Cu-Pb-Zn potentials in the upstream of Upper Gediz (TMDL-02 and TMDL-03) and Alasehir Stream Sub-Basins. The relatively higher values detected in the related stations were of natural origin and they were included in NBC evaluation. The rest of the monitoring results for Cu were assumed to be a result of anthropogenic effects.

Fe

Fe concentrations measured in nearly all of the stations were found as significantly higher than AA-EQS value of 36 μ g/L. The values changed between 200 and 76888 μ g/L. The higher values were observed in TMDL-04 (76888 μ g/L), TMDL-10 (23180 μ g/L), TMDL-22-1 (33268 μ g/L). There are kaolin and feldspar operations around Alasehir Stream; Fe potential in the inlet of Gordes Dam (TMDL-31); feldspar operation in the upstream of Demirci Stream; Fe potential near Gediz (TMDL-02). It was accepted that relatively high Fe concentrations determined in these regions are of natural origin. In rainy periods, Fe concentrations were increased indicating the effect of geological formation.

Sb

It was observed that Sb value only exceeded AA-EQS value of 7.8 µg/L in TMDL-40 station. Sb values, which was determined as relatively high in TMDL-40 station was accepted to be of anthropogenic origin, and thus not taken into consideration in NBC calculation. On the other hand, there was antimony potential in the upstream of Alasehir Stream Sub-Basin and antimony operation in the upstream of Upper Gediz Sub-Basin. Therefore, it was accepted that

Sb values were determined as relatively high in TMDL-10, TMDL-13 and TMDL-37 stations of natural origin and these stations were included in NBC evaluation.

Sn

Sn concentrations did not exceed AA-EQS value (13 $\mu g/L$) in the basin apart from TMDL-19 station (15 $\mu g/L$) located around Nif Stream. There are no tin deposits in the basin. It was determined that there were pressures with at least 2% pollution contribution in the receiving bodies, where Sn concentrations were determined to be relatively higher (TMDL-09, TMDL-37). Thus, they were accepted to be of anthropogenic origin and not assessed for NBC determination.

\mathbf{V}

V concentration measured in nearly all of the stations was found higher than 1.6 μ g/L, which is AA-EQS value. There are no vanadium deposits in the basin. It was identified that there were pressures with at least 2% contribution in the receiving bodies, in which V concentrations were determined to be relatively higher. Thus, it was accepted that the pollution in the aforementioned stations is of anthropogenic origin and were not taken into consideration for NBC evaluation.

Zn

Zn concentration measured in all of the stations was obtained higher than 5.9 μ g/L, which is AA-EQS value. The higher concentrations were observed in TMDL-04 (187 μ g/L), TMDL-10 (188 μ g/L), TMDL-12 (161 μ g/L) and TMDL-21 (185 μ g/L) stations. There has been Cu-Pb-Zn potential in the upstream of Alasehir Stream. Hence, it was accepted that TMDL-10 and TMDL-12 stations bearing relatively high Zn concentrations were under the influence of natural origins. The rest of the stations were assumed to be under the influence of anthropogenic sources and were not taken into consideration for NBC calculation.

Ti

Ti concentration was found higher than AA-EQS value of $26~\mu g/L$ in most of the stations. The higher values were detected in TMDL-04 with 2132 $\mu g/L$ and in TMDL-33 with 1260 $\mu g/L$. There is titanium potential near Ahmetli-Salihli and Gordes. The other stations were accepted to be under the influence of anthropogenic sources and were not taken into consideration for NBC calculation.

Cd

Cd concentrations were determined over $0.08\,\mu\text{g/L}$ which is AA-EQS value in all stations. The higher values were observed in Turgutlu (TMDL-15, $1.62\,\mu\text{g/L}$), Kula (TMDL-04, $1.26\,\mu\text{g/L}$) and Akhisar (TMDL-22-1, $1.13\,\mu\text{g/L}$). There are no cadmium deposits in the basin. Within the stations, it was observed that there were pressures causing pollution contribution of at least 2%, those stations were accepted to be under anthropogenic pressure and not used in NBC calculation.

Ni concentration was found higher than 4.5 μ g/L which is AA-EQS value in most of the stations. The higher values were detected in TMDL-04 with 249 μ g/L and in TMDL-22-1 with 260 μ g/L. There are nickel operations between Turgutlu and Golmarmara (around TMDL-13 and TMDL-14) and near Gordes (head of TMDL-31). Additionally, according to the groundwater monitoring studies performed by the State Hydraulic Works, Ni was determined in the upstream of Gediz Basin that referred to be naturally present. The rest of the receiving bodies (other than those mentioned above) were subjected to the pollution contribution and stations under pollution contribution of at least 2%, were accepted to be of anthropogenic origin and were not taken into consideration for NBC calculation.

Pb

Pb concentration monitored in the all receiving body stations exceeded 1.2 μ g/L which is AA-EQS value. TMDL-04 (27 μ g/L), TMDL-10 (20 μ g/L) and TMDL-22-1 (19 μ g/L) stations were observed as the most polluted sites with Pb. There are Cu-Pb-Zn potential and operation around the upstream of Alasehir Stream and Gediz. Except the related stations (TMDL-9, TMDL-10, TMDL-37, TMDL-40 and TMDL-2) located in these regions, stations which were affected by pressures with at least 2% pollution contribution were accepted to be under the influence of anthropogenic pressures.

Hg

Although there is no AA-EQS value for Hg designated with the legislation, MAC-EQS value for Hg is provided as 0.07 $\mu g/L$. According to the monitoring results, Hg concentration (excluding Nif Stream and Lower Gediz Sub-Basins) measured in the stations ranged between 0.065 $\mu g/L$ and 2.82 $\mu g/L$ in TMDL-01 and TMDL-04, respectively. The stations, which the higher Hg values are measured, are TMDL-04 (2.82 $\mu g/L$), TMDL-33 (0.76 $\mu g/L$) and TMDL-10 (0.73 $\mu g/L$). There is mercury operation and potential in the upstream of Gediz River and an old mercury establishment in the upstream of Alasehir Stream. Apart from the stations located in these regions, stations affected by the pressures with at least 2% pollution contribution were assumed to be under the influence of anthropogenic sources.

According to the obtained results, both anthropogenic pressures and geological formation have an effect on metal concentrations. Until now there are limited studies subjecting the source of metals where coming from anthropogenic activities or geological formation for Gediz Basin. The study done by Kindler and Sevim (1990) has importance for providing information about the previous source distribution of the metals in the basin. Kindler and Sevim (1990) investigated natural and anthropogenic effects of metals in sediments during the months of July-October 1988, for the Basins of Gediz, Menderes, Sakarya, Kizilirmak, Yesilirmak, Seyhan and Ceyhan. The study was undertaken with subjecting the metals of Cd. Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. For Gediz Basin 19 samples were collected at 10-20 km intervals during 320 km of Gediz River. In order to classify local anthropogenic heavy metal pollution, "index of geoaccumulation (Igeo)" was used for trace metals in sediments and their classification. Geoaccumulation index calculation was dependent on the measured concentration of the element in the fraction < 2 µm in the sediment. The classes were ranged between 0-6, that 6 means "very strong anthropogenic effect" while 0 means "practically none anthropogenic effect". According to the Igeo classification Cd, Cr, Cu, Pb and Zn was classified as 0, 2, 3, 2 and 2 respectively. In other words presence of Cr, Pb and Zn were correlated with "moderate

effect", while the presence of Cu was correlated with "moderate to strong effect" of anthropogenic pressures. The obtained values by Kindler and Sevim (1990) were 0.236 μ g/L, 232 μ g/L, 110 μ g/L, 35 μ g/L and 147 μ g/L for Cd, Cr, Cu, Pb and Zn, respectively. When the highest values of our results were compared with the previous study, it is seen that the degrees of the numbers are similar within the exception of Cd (Table 2). For Cd almost 6 times higher values were obtained in our study that could be the reason of anthropogenic sources that raised after 1990's.

Another study done by Kucuksezgin et al. (2008) investigated the distribution of Hg, Pb, Cu, Zn, Mn, Ni and Fe in the sediment, water and particulate matter and their possible sources of derivation. In this context, metals measured in surficial sediment, water and particulate matter of the Gediz River collected from 5 different points in August, October 1998, February, June 1999. According to the results, the highest values were obtained at Muradiye (corresponding to station of TMDL-29 in our study) in summer periods as a result of industrial and agricultural activities. Relatively high concentrations of Ni and Mn values measured through the origin of the basin was correlated with to geochemical composition of the sediments. In our study, similarly TMDL-29 was one of the stations that metal values were observed highly.

For comparing different methods for NBC determination, there is a study done by Oste et al. (2011) evaluating the approaches of i) clean streams, ii) erosion model, iii) sediment approach, iv) stable summer levels, v) monitoring data and vi) origin of surface water. Some criteria were used for comparison of these methods such as i) well defining natural dissolved background concentrations, ii) data necessity, iii) uncertainty, iv) elements and v) regional differentiation. According to the obtained results, all methods were evaluated as uncertain since one or more assumptions used in methods and resulted with serious limitation in deriving NBC. Among these criteria, natural dissolved background concentrations has the most significance as being the WFD focusing on. For this criteria, acceptable results were obtained for the approaches of clean stream, the sediment and the origin of surface water. The monitoring data method based on actual measurements, had the maximum score on criteria of daily data, number of elements that NBC defined and regional differentiation and this method was regarded as an acceptable fall-back alternative. The approaches of erosion model and the stable summer levels were rejected. The method of stable summer levels was found as lack of producing real NBC and also further development was required. The erosion model concentrated on natural concentrations especially on metals associated with the rock composition of the catchment area. The values obtained needed to be convert to dissolved concentrations. This conversion was not found so reliable (Oste et al., 2011).

According to the evaluation presented above, recommended NBC and Final EQS values of the metals in the inland waters are presented in Table 3. The grey colored field in the table represented the results that EQS values equivalented to EO values.

Table 3
NBC Values and Final EQS Values Recommended for Inland Waters of Gediz River Basin

	EQS Value- 1	Inland Waters	Final EQS				
μg/L	AA-EQS (μg/L)	MAC- EQS (μg/L)	NBC	AA-EQS (μg/L)	MAC-EQS (μg/L)		
Ag	1.5+NBC	1.5+ NBC	0.12	1.50	1.50		
Al	2.2+NBC	27+ NBC	2162.41	2165	2189		
As	53+ NBC	53+ NBC	33.22	53	53		
В	707+ NBC	1472+ NBC	1084.98	1792	1792		
Co	0.3+NBC	2.6+ NBC	1.66	2.0	2.6		
Cr	1.6+ NBC	142+ NBC	12.62	14	142		
Cu	1.6+ NBC	3.1+ NBC	19.52	21	23		
Fe	36+ NBC	101 + NBC	3795.80	3832	3897		
Sb	7.8+ NBC	103+ NBC	1.68	7.8	103		
Sn	13+ NBC	13+ NBC	<10	13	13		
V	1.6+ NBC	97+ NBC	9.29	11	97		
Zn	5.9+ NBC	231+ NBC	73.54	7 9	231		
Ti	26+ NBC	42+ NBC	220.22	246	262		
Cd	0.25+NBC	1.5+ NBC	0.45	0.70	1.50		
Ni	4.00+ NBC	34 + NBC	29.33	33	34		
Pb	1.20+ NBC	14 + NBC	4.11	5.3	14		
Hg	SAMPLE NE SAMPE NO.A	0.07+ NBC	0.45	SECURA	0.52		

Conclusion

This study aims to develop an approach for determination of NBC for metals in surface waters. Within this scope, 17 metals indicated in the By-law on Surface Water Quality were subjected to NBC evaluation by taking into account the effect of anthropogenic and natural sources. The pollution impact on receiving water bodies was revealed by using the seasonal monitoring data for 40 stations during 2015-2016. Both point source pressures and geologic formation were examined to understand the origin of pollution. For anthropogenic sources, monitoring was performed on industrial and urban wastewater discharges both with and without treatment plants simultaneously with the receiving body monitoring and pollution contribution of each point source on surface water was calculated. For natural sources, mining activities and geothermal source distribution were investigated.

According to the monitoring results in surface waters, nearly all metals were detected at concentrations higher than their AA-EQS within the exception of Ag, Sb and Sn. Among 17 parameters, Ag, Al, Fe, As, B and Sb were observed in surface waters as the result of natural sources. The rest of the parameters were subjected to the question of which source has an effect on their existence.

The approach for determining anthropogenic effect was a suitable way to distinguish the relative effects of the pressures on receiving bodies. This method could be beneficial to identify and compare the effect of sources, and thus help to establish critical factors for decision makers such as deciding a location of a new facility, the amount of pollution discharge of the plants and precautions for agricultural activities, especially when long-term monitoring data is not available.

By the suggested methodology, it was possible to determine NBC values for metals in surface waters. The presented method may be suitable for making general inferences with less

data, but future work is recommended that includes long-term observation. Monitoring data is required not only in receiving water body; but also, in sediment while calculating NBC. On the other hand, in future, NBC values could be determined on water body basis by taking into consideration the typology of water bodies.

Acknowledgement

This study was conducted as a part of the "Project on Application of Total Daily Maximum Load Approach to Gediz River Basin" (2015-2017) prepared by TUBITAK MRC Environment and Cleaner Production Institute under the authorization of Ministry of Forestry and Water Affairs, Directorate General for Water Management. The authors thank the General Directorate of Water Management for their guidance during study and thank Middle East Technical University, Department of Environmental Engineering for sharing their experiences.

References

- Aydin, S., & Kucuksezgin, F. (2012). Distribution and chemical speciation of heavy metals in the surficial sediments of the Bakırçay and Gediz Rivers, Eastern Aegean. *Environmental Earth Sciences*, 65,(3), 789–803
- Bizsel, N., Ardelan, M. V., Bizsel, K. C. Suzal, A. Demirdag, & A., Sarıca, D.Y. (2017). Distribution of selenium in the plume of the Gediz River, Izmir Bay, Aegean Sea. *Journal of Marine Research*, 75,(2), 81-98.
- Devlet Su İşleri Genel Müdürlüğü. (2016). Gediz Basin Groundwater Planning-Hydrogeological Survey Implementation Main Report, State Hydraulic Works 2nd Regional Directorate (in Turkish), State Hydraulic Works.
- European Commission. (2000). European Community, Water Framework Directive, 2000, Official Publication of the European Community, L327, European Parliament, Brussels
- European Commission. (2008). European Community, Directive 2008/105/EC on Environmental Quality Standards in the Field of Water Policy, 2008, European Parliament, Brussels.
- European Commission. (2010). European Commission, 2010, Technical Guidelines for the Identification of Mixing Zones pursuant to Art. 4(4) of the Directive 2008/105/EC, Brussels
- European Commission. (2011). European Commission, Common Implementation Strategy for the Water Framework Guidance Document No. 27, Technical Guidance for Driving Environmental Quality Standards.
- Kindler, F. M., & Sevim, H. E. (1990). Heavy metals in sediments of Turkish river systems—Natural background and anthropogenic effects. Retrieved from https://link.springer.com/chapter/10.1007/978-3-642-74206-432
- Kucuksezgin, F., Uluturhan, E., & Batki, H. (2008). Distribution of heavy metals in water, particulate matter and sediments of Gediz River (Eastern Aegean). *An International Journal of Environmental Monitoring and Assessment*, 141, (1–3),213–225.
- Ministry of Infrastructure and the Environment & The Ministry of Economic Affairs (1998), Dutch 4th National Water Plan, Netherlands
- MoFAL (2016). Statip Data of Gediz Basin Land Use, Ministry of Food Agriculture and Livestock.
- MoFWA (2017). Project of Implementation of the Total Maximum Daily Load Approach in the Gediz River Basin, Ministry of Forestry and Water Affairs, General Directorate for Water Management (Prepared by TUBITAK Marmara Research Center).
- MoFWA (2015). Project of Determination of Sensitive Areas and Water Quality Objectives in Turkey, Ministry of Forestry and Water Affairs, General Directorate for Water Management (Prepared by TUBITAK Marmara Research Center).
- Osté, L.A., Klein, J. & Zwolsman, G.J. (2011). Inventory and evaluation of methods to derive natural background concentrations of trace metals in surface water, and application of two methods in a case study. Deltares report, Utrecht.
- Environment Agency (2010). Estimation of background reference concentrations for metals in UK freshwaters. Final report, Edinburgh: Peters, P., Merrington, G., & Crane, M.
- Suzer, E.U., Kontaş, A., & Yılmaz, E.C. (2015). Gediz Deltası dalyan alanlarının (İzmir Körfezi) yüzey sedimentlerinde ağır metal kirliliğinin değerlendirilmesi, *Ege Journal of Fisheries and Aquatic Sciences*, 32(2), 79-87.
- Ministry of Forestry and Water Affairs. (2012). Turkish By-law on Surface Water Quality, OG: 30.11.2012/28483.
- Zuurdeeg, B.W., Van Enk, R.J., & Vriend, S.P. (1992). Natuurlijke Achtergrond gehalten van zware metalen en enkele andere sporenelementen in Nederlands oppervlaktewater. Geochem-Research, Utrecht.

Extended Turkish Abstract (Genişletilmiş Türkçe Özet)

Yüzey Sularındaki Metaller için Doğal Arka Plan Konsantrasyonlarının Belirlenmesi, Gediz Havzası Örneği

Arka plan konsantrasyonu, bir kimyasal maddenin doğal ve jeolojik proseslerden kaynaklanan miktarı olarak tanımlanmaktadır (EC, 2011). Diğer bir ifadeyle, bir alıcı ortamın, insan faaliyetleri sonucu noktasal ve yayılı kaynaklı kirleticilerin etkisi altında kalmadan, kimyasal maddenin doğal prosesler sonucu ortamda bulunmasıdır. Alıcı su ortamlarında ekolojik ve kimyasal iyi durum statüsünün sağlanabilmesi ve su kalitesinin iyileştirilebilmesi için esas oluşturan Çevre Kalite Standardı (ÇKS) belirlenirken su ortamındaki kirleticilere ait Doğal Arka Plan (DAP) konsantrasyonları büyük önem taşımaktadır. Kirleticilerin su ortamlarındaki DAP konsantrasyonları, bölgenin tipolojisi, jeolojisi, coğrafyası ve toprağının ve yeraltı suyunun fiziksel, kimyasal ve biyolojik özelliklerine göre farklılık göstermektedir.

AB Su Çerçeve Direktifindeki temel amaç tüm üye devletlerde iyi yüzey suyu statüsünü elde etmektir (WFD, 2000/60/EC). Bu amaca yönelik olarak, "öncelikli maddeler" için Komisyontarafından, "belirli kirleticiler" için üye ülkelerin kendileri tarafından su kalitesi standartları oluşturulmuştur. Üye devletler standartlara uyulamadığı durumlarda, DAP konsantrasyonlarını dikkate alabilmektedirler. Su Çerçeve Direktifi, bazı organik kirleticilerin doğal bir menşeine sahip olmasına karşın, yalnızca metaller ve yarı-metaller için DAP konsantrasyonu belirlenmesine izin vermektedir. Her ülke, DAP konsantrasyonu belirleyip belirlemeyeceğine kendi karar vermektedir.

Yüzey sularındaki metaller için DAP konsantrasyonlarının belirlenmesinde AB ülkelerinde farklı yöntemler uygulandığı görülmektedir. Bu yöntemlerde, i) temiz sulardaki metal içeriği, ii) sedimentteki metal içeriği, iii) yeraltı suyundaki arka plan konsantrasyonları, iv) uzun dönem izlenen yüzey sularındaki metal içeriği ve v) yaz döneminde (değişken olmayan) yüzey sularındaki metal içeriği dikkate alınmaktadır (Oste, et al., 2011).

Bu çalışma kapsamında Yerüstü Su Kalitesi Yönetmeliği'nde (RG: 30.11.2012/28483) yer alan metaller (Ag, Al, As, B, Co, Cr, Cu, Fe, Sb, Sn, V, Zn, Ti, Cd, Ni, Pb ve Hg) için DAP konsantrasyonlarının belirlenmesi hedeflenmiştir. Bu amaçla Gediz Havzası pilot havza olarak seçilmiştir. Havzada belirlenen yüzey suları için 2015-2016 yılları arasında, 4 dönem boyunca, 40 adet alıcı ortam istasyonu ile 29 adet kentsel atıksu ve 54 adet endüstriyel atıksu deşarj noktasında izleme yapılmıştır. Zuurdeeg ve diğ. (1992) tarafından açıklanan ve Hollanda'da uygulanan "temiz sular" yaklaşımında, DAP değeri olarak, akışın başlangıç noktasına doğru nispeten kirlenmemiş bölgedeki (memba) su kalitesi referans alınmaktadır. Çalışmada izleme yapılan noktalardan yalnızca birisinin bu tanıma uyduğu, bu noktanın da tüm havzayı karakterize etmediği sonucuna varılmıştır. İngiltere'de kullanılan "uzun dönem izlenen yüzey suları" yaklaşımında, prensip olarak en az 5 veri seti ile en az 50 istasyonun izlenmesi kabul edilmektedir (Peters ve diğ., 2010). Çalışmadaki izleme verilerinin bu anlamda yetersiz kaldığı görülmüştür. Bu sebeple, doğal ve antropojenik kaynaklar dikkate alınarak, DAP konsantrasyonun belirlendiği yeni bir yaklaşım geliştirilmesine gidilmiştir. Eldeki veriler ışığında, "temiz sular" ile "uzun dönem izlenen yüzey suları" yaklaşımları da dikkate alınarak DAP değerinin belirlendiği yöntemleri takip etmek uygun bulunmuştur. Çalışmada izleme noktalarının nispeten az kirlenmiş olanları ele alınmışve bu alıcı ortamlara etki eden baskılar incelenmiştir. Bu kapsamda, izleme çalışmaları dikkate alınarak antropojenik kaynaklar için olası her baskının kirlilik katkısı incelenmiş; ve doğal kaynaklar için madencilik faaliyetleri ile jeotermal kaynakların dağılımı değerlendirilmiştir.

Türkiye'de DAP konsantrasyonlarının belirlenmesi ile ilgili henüz bir çalışma yapılmadığı, mevcut çalışmaların daha çok yüzey sularında, sedimentte ve biyotada metallerin izlenmesi üzerine olduğu görülmektedir (Bizsel ve diğ., 2017; Suzer ve diğ., 2015; Aydin ve Kucuksezgin, 2012; Kucuksezgin ve diğ., 2008). Yüzey sularında metaller için DAP konsantrasyonunun belirlenmesini konu alan bu çalışma, Türkiye için öncü bir çalışmadır.

DAP konsantrasyonun belirlenmesinin ilk adımını, alıcı ortamda tespit edilen yüksek metal içeriğinin doğal kaynaklı mı yoksa antropojenik kaynaklı mı olduğunu belirlemek oluşturmuştur. Kirliliğin antropojenik kaynaklı olup olmadığını tespit etmek için alıcı ortamdaki izleme çalışmaları ile eş zamanlı olarak, olası noktasal kirletici kaynaklar (kentsel ve endüstriyel atıksular deşarjları) izlenmiştir. Her bir baskının, alıcı ortam üzerinde kirliliğe en az %2 oranda katkısı olanları belirlenmiş ve ardından ilgili alıcı ortamlardaki jeolojik etkisi incelenmiştir. Eğer jeolojik durum söz konusu ise DAP hesabına, incelenen alıcı ortam dahil edilmiş; değilse baskının antropojenik

olduğu kabul edilip alıcı ortam dahil edilmemiştir. Bu tespit sonrasında antropojenik baskının yoğun olduğu Aşağı Gediz Alt Havzası (Gediz Nehri mansabı ve Nif Çayı) üzerindeki istasyonlar dikkate alınmayarak kalan 27 istasyonun verilerinin incelenmesine karar verilmiştir. Noktasal baskıların alıcı ortam üzerindeki kirletici katkısının belirlenmesinde kullanılan formüller aşağıda yer almaktadır.

$$\frac{PK}{CKS}x\%100 = \% Artiş$$

PK = Proses Katkısı ÇKS = Çevre Kalite Standardı

$$\frac{[CoC]_{deg} \times Q_{deg}}{(Q_{nehir} + Q_{deg})} = PK$$

 CoC_{des} = Atıksudaki metal konsantrasyonu Q_{des} = Atıksu debisi Q_{des} = Nehir debisi

DAP değerlerinin belirlenmesinin ardından, Gediz Havzası'ndaki metallerin nihai Çevresel Kalite Standardı (ÇKS) değerlerinin belirlenmesi için aşağıdaki yaklaşım uygulanmıştır.

- DAP konsantrasyonu, ÇKS'den düşükse Çevresel Hedef (ÇH), ÇKS'ye eşittir.
 DAP<ÇKS → ÇH=ÇKS,
- DAP, ÇKS'den yüksek veya eşitse ÇH, ÇKS ile DAP'nın toplamına eşittir.
 DAP≥ÇKS → ÇH=ÇKS+DAP

Alıcı ortam istasyonlarındaki izleme sonuçları incelendiğinde, Ag, Sb ve Sn dışında neredeyse tüm metallerin yıllık ortalama değerlerinin ÇKS değerlerinin üzerinde olduğu tespit edilmiştir. DAP konsantrasyonu bulunması hedeflenen 17 metalden, Ag, Al, Fe, As, B ve Sb'nın yüzey sularında doğal kaynaklı olarak bulunduğu görülmüştür. Kalan diğer metallerin ise doğal kaynaklı veya antropojenik kaynaklı olarak yüzey sularında bulunma durumu, önerilen yaklaşıma göre incelenmiştir. Bu çalışmayla önerilen DAP konsantrasyonları belirlenmesi yaklaşımının, izleme çalışmalarında ve yalnızca Gediz Havzası özelinde değil, tüm havzalarda kolaylıkla uygulanabileceği sonucuna varılmıştır. Ayrıca bu yaklaşımla, kirliliğin kaynağının tespit edilmesi veya kirlilik katkısının belirlenmesi konularının yanı sıra, karar vericilerin hangi tesisin nerede kurulması gerektiği, hangi tesisin ne oranda kirletici deşarj edebileceği, tarımsal üretimde ne gibi önlemlerin alınması gerektiği, kullanılan zirai mücadele ilaçlarının ne oranda azaltılmasının uygun olacağı gibi kritik kararları almasında yardımcı olacağı düşünülmektedir.

Belirlenen yöntemde nispeten az veri ile genel çıkarımlar yapmak mümkündür. Ancak DAP değerinin belirlenmesi için yürütülecek yeni çalışmalarda uzun dönem ve yalnızca su ortamında değil, aynı zamanda sedimentte de izleme yapılması, ayrıca DAP değerlerinin havza geneli için tek değer olarak değil, tipolojiler dikkate alınarak su kütleleri bazında da belirlenmesi önerilmektedir.