Identification of River Basin Specific Pollutants and Derivation of Environmental Quality Standards under Water Framework Directive: Turkish Experience

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Abstract

Water Framework Directive (2000/60/EC), requires the determination of river basin specific pollutants and implementation of environmental quality standards by member states in order to reach “good water quality” in all waters.

Being a candidate for EU membership, Turkey, has conducted studies to designate the specific pollutants. In these studies, candidate chemicals were identified. Then, COMMPS and THS methods were applied for candidate chemicals. At the end, 250 specific pollutants were integrated into the national legislation with their environmental quality standards. In this way, significant progress was achieved in terms of water management and harmonization of Water Framework Directive in Turkey.

1 Introduction:

Due to intensive urban, industrial and agricultural activities, surface water resources are at risk of severe pollution. The water pollutants have various adverse effects on the aquatic organisms and humans exposed to them through different pathways (ATSDR, 2015; American Cancer Society, 2015; Bergman et al., 2013). Chemicals reaching to water resources are of concern in terms of quality of water resources. For this reason, there are many national or international regulations for control of chemicals in the environment. Besides Turkey's commitments under several multilateral environmental agreements regarding the control of chemicals, by the opening of environment chapter under European Union accession period in 2009, it has additional liabilities on the harmonization of environmental acquis of European Union including Water Framework Directive which is the main legal instrument on water management. In Water Framework Directive, chemicals of concern in the surface waters are assessed in two categories mainly as priority substances and specific pollutants. Priority substances are defined as the chemicals having the persistency, bioaccumulation and toxicity properties and they are the substances which cause significant water pollution all around the European Union. Specific pollutants are defined by Water Framework Directive (2000/60/EC), as the pollutants those are discharged to the water resources in significant amounts and causing a serious risk for aquatic organisms. Directive 2008/105/EC and Directive 2013/39/EU are the European Union legislation related to Water Framework Directive and they include provisions on the management of the priority substances in surface waters covering both inland and transitional and coastal waters. The environmental quality standards of the priority substances are given in Directive 2008/105/EC and Directive 2013/39/EU. Currently, there are 45 priority substances listed in Directive 2013/39/EU. On the other hand, specific pollutants and their environmental quality standards are designated by member states themselves depending on their economic activities and water management strategies. However, potential specific pollutant groups are described in Annex 8 to Water Framework Directive for guiding the member states. Identification and control of specific pollutants is an obligation under Water Framework Directive, in order to reach "good water status" in all waters and ensure healthy water environment for different use alternatives. Control of specific pollutants in surface waters is provided by the implementation of their environmental quality standards, which are the concentrations in water, sediment or biota which should not be exceeded to protect human health and the aquatic environment. In addition to this, Water Framework Directive requires the list of specific pollutants to be revised and updated in specific time intervals. Although there is no common methodology in European Union to identify the river basin specific pollutants, member states set down their specific pollutants by using some prioritization and screening methods.

As a candidate for EU membership, Turkey, has conducted comprehensive studies to determine the river basin specific pollutants and deriving environmental quality standards for these pollutants and specific pollutants and their environmental quality standards were integrated into the national legislation in 2016.

2 Methodology:

2.1 Establishment of the universe of chemicals:

The studies on the identification of river basin specific pollutants and derivation of the environmental quality standards started with the establishment of universe of chemicals. A wide variety of sources were handled with this aim. Scientific studies, national and international list of chemicals, the chemicals which are produced or imported in Turkey more than 1 tonnes per year, pesticides which are currently in use or used in the past, the capacity reports of industrial facilities were assessed to come up with the universe of chemicals. Furthermore, questionnaires and field studies were conducted in the pilot regions in which intensive industrial and agricultural activities are taken place.

2.2 Prioritization and Screening of Chemicals:

In the first stage of the prioritization and screening studies, the chemicals were screened according to their risk and hazard codes. The risk codes and hazard codes considered in the first stage of the screening are listed in Table 1 and 2, respectively.

Table 1: Risk codes considered in the first stage of screening

Risk Code	**Risk Code Description**
R 40	Limited evidence of a carcinogenic effect
R 45	May cause cancer
R 46	May cause inheritable genetic damage
R 50	Very toxic to aquatic organisms
R 51	Toxic to aquatic organisms
R 52	Harmful to aquatic organisms
R 53	May cause long-term adverse effects in the aquatic environment
R 60	May impair fertility
R 61	May cause harm to the unborn child
R 62	Possible risk of impaired fertility
R 63	Possible risk of harm to the unborn child
R68	Possible risk of irreversible effects
R 50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R 51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R 52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Table 2: Hazard codes considered in the first stage of screening

Hazard code	Hazard Code Description	Hazard code	Hazard Code Description
Hazards for aquatic ecosystems		**Hazards for human health**	
H400	Very toxic to aquatic life	**H341**	Suspected of causing genetic defects
H401	Toxic to aquatic life	**H350**	May cause cancer
H402	Harmful to aquatic life	**H351**	Suspected of causing cancer
H410	Very toxic to aquatic life with long-lasting effects	**H360**	May damage fertility or the unborn child
H411	Toxic to aquatic life with long-lasting effects	**H361**	Suspected of damaging fertility or the unborn child
H412	Harmful to aquatic life with long-lasting effects		
H413	May cause long-lasting harmful effects to aquatic life		

For determination of the short list of specific pollutants, risk based prioritization and screening were then applied to the chemicals listed after the first stage of screening. In these prioritization studies, Combined Monitoring and Modelling Based Priority Setting (COMMPS) and Total Hazard Score (THS) methodologies were applied.

COMMPS Methodology:

COMMPS methodology was developed by Fraunhofer Institute of Environmental Chemistry and Ecotoxicology and used for the aim of identifying priority pollutants under the Water Framework Directive (Klein et al., 1999). Both the exposure and the hazards were evaluated in this methodology. The risk score was calculated by the equation given below:

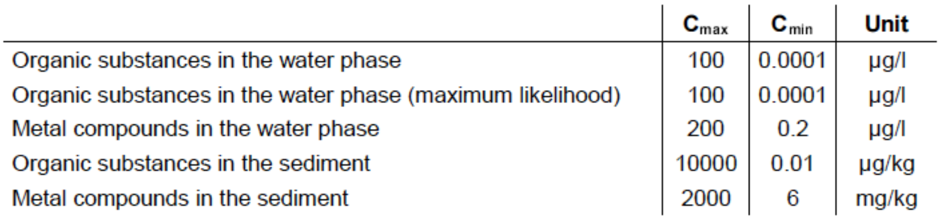
$$I\_PRIO = I\_EXP \times I\_EFF$$

Where I_EXP stands for the exposure score of the substances and I_EFF stands for the effect score of the substances.

Two different exposure scores can be calculated by this method. These are modeling based exposure score and the monitoring based exposure score. Monitoring based exposure score is calculated based on the arithmetic mean of the results in each monitoring station by the equation given below:

$$\text{I\_EXP (substance i)} = \frac{\log(C_i / (C_{min} \times 10^{-1}))}{\log(C_{max} / (C_{min} \times 10^{-1}))} * 10$$

C_i is the arithmetic mean of the analysis results and C_{min} and C_{max} are the maximum and minimum concentration values, respectively. The minimum and maximum values are given in Figure 1:



	C_{max}	C_{min}	Unit
Organic substances in the water phase	100	0.0001	µg/l
Organic substances in the water phase (maximum likelihood)	100	0.0001	µg/l
Metal compounds in the water phase	200	0.2	µg/l
Organic substances in the sediment	10000	0.01	µg/kg
Metal compounds in the sediment	2000	6	mg/kg

Figure 1: Maximum and minimum values used in calculations

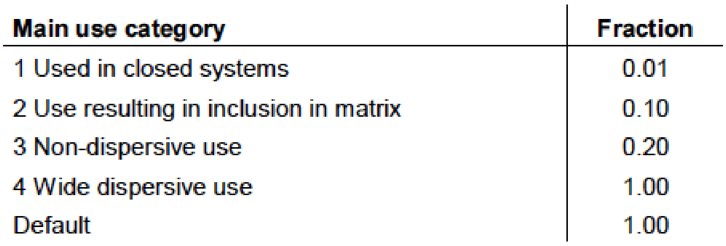
The modelling based exposure score is calculated based on the emission, degradation and dispersion by using the below equation:

$$\text{I\_EXP} = 1{,}37\,(\log(\text{EEXV}) + 1{,}301)$$

$$\text{EEXV} = \text{EMISSION x DISTRIBUTION x DEGRADATION}$$

I_EXP is normalized such that the range is between 0 and 10. The calculation of each component of this equation is as follows.

$$\text{EMISSION} = 0{,}01 \times T1 + 0{,}1 \times T2 + 0{,}2 \times T3 + 1{,}0 \times T4$$



Main use category	Fraction
1 Used in closed systems	0.01
2 Use resulting in inclusion in matrix	0.10
3 Non-dispersive use	0.20
4 Wide dispersive use	1.00
Default	1.00

Figure 2: Values used in emission factor calculation

The factor “DISTRIBUTION” represents the fraction of a chemical which partitions at equilibrium into the aquatic compartment and it is calculated by using the Mackay I Model according to the environmental characteristics given in the model (Mackay, 2001). By this model, fugacity (f) of the chemicals in each environmental compartment can be calculated. Fugacity is the tendency of a chemical to escape from a system. The model requires the calculation of fugacity capacity (Z) for each compartment and the fugacity is related to the concentration of the chemical in the environmental compartments.

$$C=Zf$$

$$\text{Air (1) } Z1 = 1/RT$$

$$\text{Water (2) } Z2 = CS/VPS$$

$$\text{Soil (3) } Z3 = Z2\ n_3 foc_3\ K_{oc} / 1000$$

$$\text{Sediment (4) } Z4 = Z2\ n_4 foc_4\ K_{oc} / 1000$$

$$\text{Susp. Solids (5) } Z5 = Z2\ n_5 foc_5\ K_{oc} / 1000$$

$$\text{Fish (Biota) (6) } Z6 = Z2\ n_6\ L\ K_{ow} / 1000$$

R : Gas constant (8.314 J/mol K)

T : Temperature (K)

Cs : Water solubility (mol/m3)

VPs : Vapour pressure (Pa)

n_i : Density of phase i (kg/m3)

foc_i : Mass fraction of organic carbon in phase i

L : Lipid content in fish (0.10)

K_{oc} is derived from K_{ow} according to Mackay model: $_{Koc}$ = 0.41

The environmental characteristics defined in Mackay I Model are given in the figure below (Mackay, 2001):

Compartment	Air	Water	Soil	Sediment	Suspended Solids	Fish (Biota)
Volume (m^3)	10^{14}	$2x10^{11}$	$9x10^9$	10^8	10^6	$2x10^5$
Depth (m)	1000	20	0.1	0.01	-	-
Area (m^2)	$10x10^{10}$	$10x10^9$	$90x10^9$	$10x10^9$	-	-
Fraction oc (f_{oc})	-	-	0.02	0.04	0.2	-
Density (kg/m^3)	1.2	1000	2400	2400	1500	1000

Figure 3: Environmental characteristics defined in Mackay I model

The factor "DEGRADATION" assumed depending on the biodegradability of the substances. The values used are given below:

Biodegradability	Factor
Ready biodegradable	0.1
Inherent biodegradable	0.5
Persistent	1.0
Default	1.0

Figure 4. Values used as degradation factor

The effect score is calculated according to the equation shown below:

$$I\_EFF = EFS_d\ (5) + EFS_i\ (3) + EFS_h$$

Where EFS_d stands for the direct aquatic effect score, EFS_i for indirect aquatic effect score and EFS_h for human health effect score.

$$EFS_d \text{ (substance i)} = \frac{\log (PNEC_i /(10 \times PNEC_{max}))}{\log (PNEC_{min} /(10 \times PNEC_{max}))} \times WF$$

WF is the weighting factor for direct effects (5 for organic substances, 8 for metals). The PNEC values used are:

	$PNEC_{max}$	$PNEC_{min}$	Unit
organic substances in the water phase	1	0.000001	mg/l
organic substances in the sediment (see chap. 5.2)	10	0.000001	mg/kg
metal compounds in the water phase (see chap. 5.3)	0.1	0.000001	mg/l

Figure 5: Maximum and minimum PNEC values

EFS_i is determined according to the criteria given in Figure 6:

$logP_{ow}$		Molecular Weight	Bioconcentration Factor (BCF)	Scores
< 3	or	> 700	< 100	0
3 <= log Pow < 4	and	< 700	100 - < 1000	1
4 <= log Pow < 5	and	< 700	1000 - < 10000	2
>= 5	and	< 700	> 10000	3
default (no logPow)	and	< 700	no BCF	3

Figure 6. Criteria of determining indirect aquatic effect score (EFS_i)

EFS_h is determined according to the criteria given in Figure 7:

Carcinogenicity	Mutagenicity	Effects on Reproduction	Chronic Effects (oral)	Scores
R45	R46	R47, R60 or R61	-	2
R40	R40	R62, R63 or R64	-	1.8
-	no test	no test	R48 in any combination with R23 - R28	1.4
-	-	no test	R48 in any combination with R20 - R22	1.2
-	-	-	R33	1
-	-	-	-	0

Figure 7: Criteria of human health effect score (EFS_h)

The maximum risk score calculated is 100 by COMMPS methodology. There is no cutoff criteria defined for the evaluation of risk scores and this is a shortcoming of the COMMPS methodology.

THS Methodology:

The original methodology is developed in UK to propose an alternative screening tool for the identification of priority pollutants under Water Framework Directive (Daginnus et al., 2011). The methodology consists of both hazard and exposure assessment. However, due the data gaps on environmental levels of chemicals, only hazard assessment was considered in these studies. The equation used for the hazard score calculation is given below:

$$THS= P+B+T+ED$$

where P stands for Persistent (no persistence = 0, persistent = 1), B for Bioaccumulative (no bioaccumulation = 0, bioacumulative = 1), T for Toxic (no toxicity = 0, toxic = 1) and ED for being in the Endocrine Disruptors list Categories 1 and 2 (no ED activity = 0, ED = 1). An additional +1 was added to the total score if the substance fulfilled all the screening criteria or if the substance was classified as vPvB (v = very). The cutoff values used in the studies are:

P=1 if half life in water>40 days

B=1 if BCF>2000, if BCF>5000 then vB

T=1 if NOEC<0.01 mg/L or E(L)C_{50}<0,1 mg/L

Therefore, the maximum hazard score is 4 which corresponds to a substance classified as PBT or vPvB, while the minimum score is 0.

2.3 Derivation of EQSs

For EQS derivation, detailed literature survey were done to collect acute (i.e. LC_{50}, EC_{50}) and chronic (i.e. NOEC) ecotoxicological data of chemicals for 3 trophic levels (i.e. daphnia magna, algae and fish) and surface water EQSs were calculated by deterministic and/or probabilistic method (ETX 2.0 Software) in line with the procedures given in the Technical Guidance Document No.27 of 2000/60/EC Water Framework Directive (European Commission, 2011). During these studies, data sources for the collection of ecotoxicological data of chemicals are EPA Ecotox Database, TOXNET Database, EU Risk Assessment Reports and material safety data sheets. Thanks to deterministic and probabilistic methods, both annual average (AA-EQS) and maximum (MAC-EQS) EQSs were calculated.

Deterministic Method:

In deterministic method, the lowest EC_{50} or LC_{50} value is taken and divided by the assessment factor (AF) changing between 1 and 10000 and given in the Technical Guidance Document No.27 of 2000/60/EC Water Framework Directive based on the number of acute toxicological data gathered from the literature. Similarly, the same procedure is followed for the calculation of AA-EQS from the chronic toxicological data considering the lowest NOEC value. In this approach, AF can be thought as the indicator of uncertainties in the available data.

In this method, in the process of derivation of EQS, AF values differ according to the number of data, data type and type of the organisms that data is originated from. The reason is that the difference between the chemical sensitivity of the marine species is much more apparent and there is an uncertainty coming from whether the species living in marine environment are represented in the data set. Therefore, by having higher AF values, EQS values are generally lower and stricter for salt waters compared to the freshwaters (European Commission, 2011).

In this method, regardless of whether data is combinable or not, AF values are determined separately for fresh and salt waters. In this scope, for MAC-EQS, in the process of determining AF, Table 3.4, represented in Technical Guidance Document No.27, is used for freshwater while Table 3.5, represented in the Document, is used for salt water (European Commission, 2011).

Probabilistic Method:

Probabilistic method is based on species sensitivity distribution (SSD) modeling in which all reliable toxicity data are ranked and a model fitted. By this method, the threshold level that represents a safe concentration of the substance which thereby protects most organisms (typically 95%), namely hazardous concentration (i.e. HC5), is calculated with the log-normal distribution of data and then this value is divided by the AF ranging between 1 and 5 based on the available toxicological data. This method can be applied if and only the number of available data for 3 trophic levels is equal or greater than 10. ETX 2.0 Software can be used for the EQS calculation by this method (Aldenberg and Jaworska, 2000). This method is more reliable than the deterministic method due to running with lower AF value; therefore; it should be preferred for EQS calculation when there are available sufficient data.

Rationale behind SSD by ETX 2.0 Software:

ETX 2.0 Software uses the method of Aldenberg and Jaworska (2000) for HC5 calculation.

$$\text{Log HC5} = X_m - k \times s$$

Where:

Xm: mean of log-transformed data

k: extrapolation constant depending on protection level and sample size (according to Aldenberg and Jaworska, 2000)

s: Standard deviation of log-transformed data

$$\text{EQS} = \text{HC5} / \text{AF} \qquad (\text{AF: } 1\text{-}5)$$

According to fraction affected (%), there is a table giving the value of k constant based on the number of toxicity data available. Rows are sample sizes, columns are fraction affected in this table. There are 6 sets of fraction affected as 1%, 2%, 5%, 10%, 25% and 50%. Sample size changes between 2 and infinity. “k” value is independent of the substance involved (Aldenberg and Jaworska, 2000).

According to the Guidance Document, an AF of 5 is used by default but it may be reduced where evidence removes residual uncertainty. The exact value of the AF depends on an evaluation of the uncertainties around the derivation of the HC5. Generally, the number of data used in HC5 derivation is taken as a baseline and different AFs between 1 and 5 are designated depending on the number of available data. In these studies, AFs were determined based on the considerations in Table 1.

Table 3: AF values for probabilistic method

Number of Data	AF
10-15	5
16-20	4
21-25	3
26-30	2
> 30	1

3 Results and Discussions:

In scope of this study, a universe of chemicals including 3762 chemicals was assessed initially. As stated in the methodology part, risk and hazard codes were considered in the first stage of the screening and 2957 chemicals were removed from the list. On the other hand, 34 chemicals including metals, PAHs and PCBs were directly added to the final list without any screening. The remaining 805 chemicals were then prioritized by using COMMPS and THS methods depending on the availability of data on the annual production amount. When the production amount data was available, COMMPS method was implemented and the THS method was applied otherwise.

Among this list, 541 chemicals were prioritized by using the COMMPS method and the 230 chemicals were prioritized by using the THS method. The chemicals having a score greater than 3 in THS method were included in the final list. However, there was no predefined cutoff criteria for the COMMPS score. In this study, considering the distribution of scores of chemicals, the cutoff value was determined as 0. According to these assessments, 117 point sourced and 133 diffuse sourced specific pollutants were determined and EQSs were derived for these pollutants. Specific pollutant list includes heavy metals, halogenated organics, endocrine disrupters, aromatic hydrocarbons and pesticides. These prioritization results demonstrated that extend of monitoring and inventory studies for chemicals must be enhanced so that more reliable and realistic assessments can be obtained in the future. Moreover, deterministic method was applied for majority of chemicals for EQS calculations. Acute toxicological data were dominant to chronic toxicological data in literature. This resulted in higher uncertainties in derived AA-EQS values. Future studies might focus on gathering chronic toxicity data for different taxonomic groups.

Currently, national specific pollutants and their AA-EQS and MAC-EQSs in fresh water and saline waters were adapted to By-Law on Surface Water Quality and published on 10th August 2016 officially. By that date, it became possible to monitor and control these pollutants in surface waters in line with the Water Framework Directive and to take necessary precautions in time in order to protect and improve surface water quality when there is an identified risk of not attaining water quality objectives. Using the outcomes of upcoming monitoring studies, the specific pollutant list will be updated according to Water Framework Directive requirements.

4 Conclusions:

Comprehensive studies were accomplished in Turkey for the determination of river basin specific pollutants and their environmental quality standards in water column, sediment and biota. In the context of these studies, an interdisciplinary and multi-stakeholder approach was adopted. Scientific, governmental and professional studies were taken into the consideration and the chemicals which should be regulated in water resources were identified with the aim of designating the river basin specific pollutants under the Water Framework Directive.

While determining the specific pollutants, COMMPS and THS methods were applied. By these methods, chemicals were ranked according to their usage amount, physicochemical properties, toxicity, potential to be present in wastewater, and environmental fate. The outputs obtained by these methods were combined and 117 point-sourced and 133 diffuse-sourced specific pollutants were assigned at national basis.

In order to derive the environmental quality standards for specific pollutants, acute and chronic toxicity data was collected from the literature and assessed by deterministic and probabilistic methods. Results showed that there was lack of ecotoxicological data from three trophic levels for some of the chemicals. This situation made the derivation of EQS values for these chemicals impossible.

The specific pollutants and the corresponding environmental quality standards were incorporated into By-Law on Surface Water Quality Management in 2016. According to the provisions of the by-law, environmental quality standards for specific pollutants must be met by the end of 2019. Therefore, monitoring programs including specific pollutants have been prepared for 25 river basins. Currently, efforts are put to reveal the measures to achieve the environmental quality standards. The study is an outstanding example of bridging science and policy in water quality management since it directly makes use of the outcomes of scientific studies in policy making.

References:

Aldenberg, T., Jaworska, J.S. (2000). Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. *Ecotoxicology and Environmental Safety.* 46 (1), 1-18.

American Cancer Society (ACS). Known and probable human carcinogens. Available from: http://www.cancer.org/cancer/cancercauses/othercarcinogens/generalinformationaboutcarcinogens/known-and-probable-human-carcinogens [Accessed: 16th January 2016]

ATSDR. Health effects of chemical exposure. Available from: http://www.atsdr.cdc.gov/emes/public/docs/Health%20Effects%20of%20Chemical%20Exposure%20FS.pdf [Accessed: 16th January 2016]

Bergman, A., Heindel, J.J., Jobling, S., Kidd, K.A., Zoeller, R.T. (2013). State of the science of endocrine disrupting chemicals. UNEP &WHO.

Daginnus, K., Gottardo, S., Payá-Pérez, A., Whitehouse, P., Wilkinson, H., Zaldívar, J. (2011). A model-based prioritisation exercise for the European Water Framework Directive. *Int. J. Environ. Res. Public Health*, 8, 435-455.

Directive 2013/39/EU (Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy)

Environmental Quality Standards Directive, 2008/105/EC. (Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council)

EPA Ecotox Database. Available from: http://cfpub.epa.gov/ecotox/ [Accessed: 16th October 2016]

European Commission. (2011). WFD CIS Guidance Document No. 27. Technical Guidance for Deriving Environmental Quality Standards. ISBN: 978-92-79-16228-2, DOI: 10.2779/43816.

Klein, W., Denzer, S., Herrchen, M., Lepper, P., Müller, M., Sehrt, R., Strom, A., Volmer, J. (1999). Revised Proposal for a List of Priority Substances in the Context of Water Framework Directive (COMMPS Procedure). Germany: Fraunhofer Institute of Environmental Chemistry and Ecotoxicology.

Mackay, D. (2001). Multimedia environmental models: the fugacity approach. Lewis Publishers

Ministry of Forestry and Water Affairs. (2013). Project on Control of Hazardous Substances Pollution (TMKK). Final Project Report. Ankara: Turkey.

Ministry of Forestry and Water Affairs. (2014). Project on Determination of Hazardous Substances in Coastal and Transitional Waters and Ecological Coastal Dynamics (KIYITEMA). Final Project Report. Ankara: Turkey.

Ministry of Forestry and Water Affairs. (2014). Project on Detection of Water Pollution Resulted from the Use of Plant Protection Products and Derivation of Environmental Quality Standards. Final Project Report. Ankara: Turkey.

TOXNET Database: Available from: https://toxnet.nlm.nih.gov/ [Accessed: 15th October 2016]

Turkish By-Law on Surface Water Quality. Official Gazette: 28483, 30.11.2012.

Water Framework Directive, 2000/60/EC (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a Framework for Community Action in the Field of Water Policy)