

DETERMINATION OF ENVIRONMENTAL QUALITY STANDARD - BASED
DISCHARGE LIMITS AND MIXING ZONES FOR TERSAKAN SUB-BASIN OF
YEŞİLIRMAK RIVER

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

SARP ÇELEBİ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

SEPTEMBER 2019

Approval of the thesis:

**DETERMINATION OF ENVIRONMENTAL QUALITY STANDARD -
BASED DISCHARGE LIMITS AND MIXING ZONES FOR TERSAKAN
SUB-BASIN OF YEŞİLIRMAK RIVER**

submitted by **SARP ÇELEBİ** in partial fulfillment of the requirements for the degree
of **Master of Science in Environmental Engineering Department, Middle East
Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Bülent İçgen
Head of Department, **Environmental Eng.**

Prof. Dr. Kahraman Ünlü
Supervisor, **Environmental Eng., METU**

Examining Committee Members:

Prof. Dr. Ülkü Yetiş
Environmental Engineering, METU

Prof. Dr. Kahraman Ünlü
Environmental Eng., METU

Prof. Dr. Filiz B. Dilek
Environmental Engineering, METU

Dr. Yasemin Dilşad Yılmaz Tokel
Environmental Engineering, METU

Assoc. Prof. Dr. Gökşen Çapar
Ankara University, Institute of Water Management

Date: 13.09.2019

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Surname: Sarp Çelebi

Signature:

ABSTRACT

DETERMINATION OF ENVIRONMENTAL QUALITY STANDARD - BASED DISCHARGE LIMITS AND MIXING ZONES FOR TERSAKAN SUB-BASIN OF YEŞİLIRMAK RIVER

Çelebi, Sarp
Master of Science, Environmental Engineering
Supervisor: Prof. Dr. Kahraman Ünlü

September 2019, 146 pages

The control of point source discharges to rivers has become more elaborate since the establishment of environmental quality standards (EQSs). Many countries including Turkey have set EQS values for various contaminants of concern (CoCs) i.e. maximum concentration limits that would not cause detrimental effects on the health of the human-beings or the overall environment. One important challenge of achieving these EQSs is to reconcile the effluent limits that are technically and economically achievable with the ones that are required to accomplish the EQSs. Tersakan Sub-basin of Yeşilırmak River acquires good examples of this challenge due to the intense industrial and agricultural activities present. In this study, an approach to help this compromise is developed and implemented for all suitable discharge points within the sub-basin. The foundation of this approach is that effluent discharges may mix and become diluted within negligibly short distances from the point of discharge where exceedance of EQSs can be permissible. The approach developed, modularly combines different analytical solutions of the advective-dispersive mass transport equation that are applicable under different mixing conditions and estimates maximum allowable discharge concentrations of CoCs. The results of the case study which included all 20 instances, indicate that none of these discharges need load reduction

to achieve EQSs. However, in various points tridecane, nickel, bis(2-ethylhexyl) terephthalate, NH₄-N, total phosphorus, and free CN have consumed $\geq 10\%$ of their discharge quotas estimated by the mentioned approach. Therefore, these six CoCs and their corresponding two discharge points may require more attention in the future.

Keywords: Mixing Zone, Discharge Limit, Yeşilırmak River, Water Quality Modeling, Mass Transport in Rivers

ÖZ

YEŞİLIRMAK NEHRİ'NİN TERSAKAN ALT HAVZASI İÇİN ÇEVRE KALİTE STANDARTLARI TEMELLİ DEŞARJ LİMİTLERİ VE KARIŞIM BÖLGELERİ BELİRLENMESİ

Çelebi, Sarp
Yüksek Lisans, Çevre Mühendisliği
Tez Danışmanı: Prof. Dr. Kahraman Ünlü

Eylül 2019, 146 sayfa

Çevresel Kalite Standartlarının (ÇKS) kabulünden itibaren akarsulara yapılan noktasal deşarjların kontrolü daha ayrıntılı hale gelmiştir. Türkiye de dahil birçok ülke çeşitli dikkate değer kirleticiler (DDK) için ÇKS değerleri, yani insanların veya genel olarak çevrenin sağlığına zararlı etkilere sebep olmayacak maksimum konsantrasyon sınırları belirlemiştir. Bu ÇKS'leri sağlamanın önemli bir zorluğu teknik ve ekonomik olarak ulaşılabilir olan atıksu sınır değerleriyle ÇKS'lere erişmek için gerekli olan sınır değerleri uzlaştırabilmektir. Yeşilırmak Nehrinin Tersakan alt havzası, mevcut yoğun sınai ve tarımsal faaliyetleriyle bu zorluğun iyi örneklerini barındırmaktadır. Bu çalışmada, bu uzlaşmaya yardımcı olacak bir yaklaşım geliştirilerek alt havza bünyesinde bulunan tüm elverişli noktalarda uygulanmıştır. Bu yaklaşımın temelinde atıksuların, ÇKS aşımının izin verilebilir olabileceği, deşarj noktasından ihmal edilebilir ölçüde kısa mesafelerde karışarak seyrebilmesi yatmaktadır. Geliştirilen yaklaşım advektif-dispersif kütle taşınımı denkleminin farklı karışım koşullarında uygulanabilir olan farklı analitik çözümlerini modüler bir biçimde bir araya getirmekte ve DDK'ler için izin verilebilir maksimum deşarj konsantrasyonu tahminleri yapmaktadır. 20 örneği içeren vaka çalışmasının sonuçları, hiçbir deşarjın ÇKS'leri sağlayabilmek için yük azaltmaya ihtiyacı olmadığını göstermektedir. Ancak farklı

noktalarda tridekan, nikel, bis(2-etilhekzil) tereftalat, $\text{NH}_4\text{-N}$, toplam fosfor ve serbest CN mevzu bahis yaklaşımla vasıtasıyla ölçülen deşarj kotalarının $\geq 10\%$ 'unu doldurmuş durumdadır. Dolayısıyla bu altı DDK ve bunlara ilişkin iki deşarj noktası gelecekte daha çok dikkat gerektirebilecektir.

Anahtar Kelimeler: Karışım Bölgesi, Deşarj Limiti, Yeşılırmak Nehri, Su Kalitesi Modelleme, Nehirlerde Kütle Taşınımı

To all who strive to serve humanity

ACKNOWLEDGEMENTS

This journey has been long and rough with many unexpected, sharp turns. Many big decisions on behalf of me had to be made in the past three years. It was not easy and still remains not. But it was worth every drop of blood, sweat and tear all thanks to the amazing people that I am surrounded with.

Undoubtedly, first of all, I would like to express my deep gratitude for my thesis advisor Prof. Dr. Kahraman Ünlü, who has been a mentor for me with his unique balance of joy, sincerity, fatherly understanding, intellect and rigor since my time as an undergraduate student. I regard having the opportunity to work alongside him an honor and a blessing.

Secondly, all the faculty members of our department, most of whom I had somehow crossed paths with, deserve a heart-felt appreciation. I have learnt so much and continue to learn more from each of them. Not one of them has ever rejected me when I had questions since my last 8 years of being a student here and almost two years of my assistantship. However, I still feel the need to explicitly mention a few names who have taken more trouble accompanying me so far; therefore I especially thank Prof. Dr. Ülkü Yetiş, Prof. Dr. Filiz B. Dilek, and Prof. Dr. Bülent İçgen for their patient support.

Then, I should show my sincere love and gratefulness to all of my colleagues both from my first ever workplace, which is the Graduate School of Natural and Applied Sciences of our university and from the Department of Environmental Engineering where has been almost like a second home for me for almost a decade now. I would specifically like to thank Prof. Dr. Gülbin Dural who has been my first superior at a workplace, and I have been much inspired by her intelligence, honesty and wise humility; and all my kind and cooperative colleagues namely, Yeliz Galioğlu, Melda İşler Binay, Satı Burhanlı, Ece Hocaoglu, Fulya Karahan Dağı, Esra Tüzün and Ayşegül Karabulut from the GSNAS, my former roommates and “comrades” Cansu

Demir and Ceren Ayyıldız, my current roommates Berkay Çelebi and Merve Tanrikulu, my dear friend Tercan Çataklı, my past and present “hocam” Zeynep Özcan from whom I have learnt a lot since I have started working as assistant at the department as well, and Kumru Kocaman who has proven to be a very dear friend with her sincere support during the bad days. I also would like to thank our secreteries Gülçin Şahin and Güldane Kalkan, who are always ready and willing to help.

This study has been directly supported by many others as well. It should be acknowledged that many of the efforts shown for this study was supported by TÜBİTAK (the Scientific and Technological Research Council of Turkey), under project number 115Y013. I have to thank Prof. Dr. Ubeyde İpek, the honorable president of Munzur University, and a researcher in the project, whom directed us to two hard-working military personnel Col. Abdullah Değer and Lt. Hakan Şahin at the General Command of Mapping who had undeniable contributions to the study.

For my many endless and sleepless nights and long hours of steady work, I would like to thank our tea farmers in the Black Sea region, the coffee farmers from the tropical lands, and the awe-inspiring musicians who have all together been producing the fuel for this study.

Of course, I have a great thankfulness and gratitude for my closest friends and dear family, for always believing in me more than I could ever believe in myself and being there for me at the darkest of the dark times. This relief and happiness belong to all of us, especially to my mother Ayfer Akay Çelebi, my father Nuşan Çelebi, my beloved twin sister Gökçe Çelebi, and my new family Süheyla, Burhan and Ali Rıza Arıbaş, and our deeply loved little ones Bacaksız and Pekmez.

Above all, at the highest summit, I would like to thank my incredibly loving, caring, soothing and supportive wife Elçin Çelebi. She is the primary sponsor of all my endeavors and has been there literally the whole time. My gratefulness is beyond words, and I hope this has been easier for her than it was for me. Because it has been easier for me thanks to her.

TABLE OF CONTENTS

ABSTRACT	v
ÖZ	vii
ACKNOWLEDGEMENTS.....	x
TABLE OF CONTENTS	xii
LIST OF TABLES.....	xv
LIST OF FIGURES	xvii
LIST OF ABBREVIATIONS.....	xix
LIST OF SYMBOLS	xxi
1. INTRODUCTION.....	1
2. LITERATURE SURVEY	5
2.1. Concepts of River Water Quality.....	5
2.2. River Water Quality Monitoring.....	9
2.3. Point Source Pollution Control in Rivers	14
2.3.1. Discharge Standards or Best Available Techniques Associated Emission Limits (BAT-AELs)	15
2.3.2. Environmental Quality Standards (EQSs).....	17
2.3.3. Discharge Limits and Mixing Zones	20
2.3.4. European Commission's Tiered Approach	22
2.3.5. European Commission's Discharge Limit Software	26
2.3.6. Precautions to Reduce the Mixing Zone	29
3. MATERIALS AND METHODS	33
3.1. Information about the Study Site	33

3.2. Data Collection and Preparation.....	43
4. A NOVEL APPROACH TO DISCHARGE LIMIT ESTIMATION	57
4.1. Mass Transport Processes in Rivers.....	58
4.1.1. Advection.....	59
4.1.2. Molecular Diffusion.....	59
4.1.3. Turbulent Diffusion	60
4.1.4. Shear Dispersion	60
4.1.5. Relationships for Dispersion Coefficients	60
4.2. Estimation of Mixing Zones	65
4.3. Characteristic Mixing Distances	68
4.4. Establishment of Discharge Limits	69
5. RESULTS AND DISCUSSION	81
5.1. Discussion on Hydro-geometric and Hydraulic Data from Tersakan Sub-Basin ..	81
5.2. Discharge Limit Establishment for Point Source Discharges in Tersakan Sub-Basin ..	84
5.3. Estimation of Analytical-Solution-Based Mixing Distances	93
5.4. Relationships Related to Mixing Distances.....	97
5.5. Relationship Between Peclet Numbers and River Width to Depth Ratios.....	105
5.6. Advantages and Limitations of the Discharge Limit Establishment Approach.	108
5.7. Applicability in Turkey.....	109
6. SUMMARY, CONCLUSIONS & RECOMMENDATIONS	111
6.1. Summary and Conclusions	111
6.2. Recommendations for Further Studies	116
REFERENCES.....	119

APPENDICES

A. MATLAB CODES FOR THE DISCHARGE LIMIT ESTABLISHMENT APPROACH.....	123
B. MATLAB CODES FOR THE ESTIMATION OF HYDRO-GEOMETRIC, HYDRODYNAMIC AND MIXING PARAMETERS OF RECEIVING WATER BODIES	135

LIST OF TABLES

TABLES

Table 2.1. Distribution of Earth's water resources [4], [5]	5
Table 2.2. Table of sectors covered in European Commission's BREF documents and their current status [26]	18
Table 2.3. Maximum permissible process condition values for rivers [30].....	23
Table 2.4. Details about each worksheet included in the Discharge Test software which is programmed as an MS Excel Workbook.....	28
Table 3.1. Major industries located within Tersakan Creek sub-basin	34
Table 3.2. Details about receiving water body (RWB) and discharge monitoring stations (MSs) within Tersakan sub-basin	38
Table 3.3. Monitoring station couples within Tersakan sub-basin that are suitable for discharge limit estimation studies	43
Table 3.4. Values of measured width (w) and calculated mean velocity (v), depth (d), width/depth ratio (w/d), cross-sectional area (A) and flowrate (Q) for receiving water body monitoring stations within Tersakan sub-basin (season-wise).....	47
Table 3.5. Values of measured width (w) and calculated mean velocity (v), depth (d), width/depth ratio (w/d), cross-sectional area (A) and flowrate (Q) for receiving water body monitoring stations within Tersakan sub-basin (average)	48
Table 3.6. Channel slope values for each receiving body monitoring station within Tersakan sub-basin.....	49
Table 3.7. Estimations obtained for shear velocity (u^*), longitudinal dispersion coefficient (D_x), transverse dispersion coefficient (D_y), vertical shear dispersion coefficient (K_z), vertical characteristic mixing distance (L_z), transverse characteristic mixing distance (L_y) and Pe for receiving water body monitoring stations along Tersakan Creek (season-wise)	50
Table 3.8. Estimations obtained for shear velocity (u^*), longitudinal dispersion coefficient (D_x), transverse dispersion coefficient (D_y), vertical shear dispersion coefficient (K_z), vertical characteristic mixing distance (L_z), transverse characteristic	

mixing distance (L_y) and Pe for receiving water body monitoring stations along Tersakan Creek (average)	51
Table 3.9. Details about the 20 particular discharges that are suitable for discharge limit estimation studies within the Tersakan sub-basin (average)	53
Table 3.10. Half-lives and first-order biodegradation constants for the CoCs observed within Tersakan sub-basin that can be found in the literature	54
Table 3.11. Advective and dispersive Damkohler numbers (Da^I and Da^{II} , respectively) related to selected CoCs found to be suitable for discharge limit establishment in Merzifon OIZ discharge	55
Table 4.1. Analytical solutions of the advective-dispersive mass transport equation under different conditions	73
Table 5.1. Relevant receiving water body hydro-geometric and mixing parameters associated with the four receiving water body monitoring stations that are suitable for discharge limit estimation applications	84
Table 5.2. Discharge limits, discharge quota usage percentages and other relevant information about the 20 discharge cases that are suitable for discharge limit estimation applications within Tersakan sub-basin	88
Table 5.3. End-of-pipe discharge standards set for mixed industrial WWTPs taken from the Water Pollution Control Regulation of Ministry of Environment and Urbanization of the Republic of Turkey (Table 19 in the regulation's appendix) [27]	91
Table 5.4. Part of all 20 discharges within Tersakan sub basin that have end-of-pipe discharge standards set in the Turkish Water Pollution Control Regulation with their discharge concentrations, relevant end-of-pipe discharge standard values and violation status	92
Table 5.5. ASB and E-ToD mixing distances ($L_{y,ASB}$ and $L_{y,E-ToD}$) and their ratios, with the CoC concentration values associated with them, river CoC concentrations (C_w) and CoC discharge limit concentrations (C_{DL}) respectively and their ratios for all 20 specific cases within Tersakan sub-basin	98
Table 5.6. ASB, E-ToD mixing distances ($L_{y,ASB}$ and $L_{y,E-ToD}$), river width (w), $10 * w$ river width, and ratios for $10*w$ per ASB and E-ToD mixing distances.....	101
Table 5.7. Relevant information for the expanded investigations about the relationships of mixing distances for all receiving water body stations within Tersakan sub-basin	103

LIST OF FIGURES

FIGURES

Figure 2.1. Water quality monitoring program stages [16].....	13
Figure 2.2. Chart that shows the current conditions of BREF documents prepared by the European Commission	17
Figure 2.3. A summary diagram for all steps of the Tiered Approach	25
Figure 3.1. A map showing Tersakan sub-basin drainage network and the receiving water body and discharge monitoring stations.....	36
Figure 3.2. All receiving water body and discharge monitoring stations located within Tersakan sub-basin that at least one set of monitoring data have been collected	37
Figure 3.3. Flowrate approximation.....	45
Figure 3.4. Cross-sectional area approximation.....	46
Figure 3.5. A chart showing the suitability of the concentrations of the 19 CoCs in the receiving water body and the discharge the five receiving water body-discharge monitoring station couples previously selected	52
Figure 4.1. A depiction of the mixing processes that take place in river after an effluent discharge	58
Figure 4.2. An illustration about the extent of mixing zones.....	67
Figure 4.3. Flow diagram of the EQS-based discharge limit establishment approach developed	79
Figure 5.1. The percent increase and decrease of receiving water body hydro-geometric, hydrodynamic and mixing parameters according to high and low flowrate seasons as compared to the average values.....	83
Figure 5.2. Future risk distributions associated with the 20 discharge cases within Tersakan sub-basin.....	89
Figure 5.3. Tridecane concentration vs. Longitudinal distance graph with initial longitudinal distance guess equal to 20 m for Merzifon OIZ discharge	95

Figure 5.4. Tridecane concentration vs. Longitudinal distance graph with initial longitudinal distance guess equal to 100 m for Merzifon OIZ discharge.....	95
Figure 5.5. Tridecane concentration vs. Longitudinal distance graph with initial longitudinal distance guess equal to 50 m for Merzifon OIZ discharge (The arrow shows the longitudinal extent of the ASB mixing zone)	96
Figure 5.6. Tridecane concentration vs. transverse distance with initial longitudinal distance guess equal to 50 m for Merzifon OIZ discharge	97
Figure 5.7. R_{Ly} (ratios of mixing distances) vs. R_C (ratios of CoC concentrations)	100
Figure 5.8. E-ToD mixing distances vs. $10 * \text{width}$ values for the 20 cases within Tersakan sub-basin	102
Figure 5.9. Ratio of mixing distances (R_{Ly} , E-ToD to ASB) vs. ratio of CoC discharge concentrations (R_C , discharge limit to discharge concentration) and R_C^2 in a graph with two x-axes.....	104
Figure 5.10. E-ToD mixing distances vs. “ $10 * \text{river width}$ ” values for all the 14 receiving water body monitoring stations within Tersakan sub-basin	105
Figure 5.11. Pe vs. w/d ratio graph with relevant equations and R^2 values for various fits for the 20 discharge cases within Tersakan sub-basin that are suitable for discharge limit estimation applicatios.....	107
Figure 5.12. Pe vs. w/d ratio graph with relevant equations and R^2 values for various fits for all 14 receiving water body monitoring stations within Tersakan sub-basin	107

LIST OF ABBREVIATIONS

ABBREVIATIONS

A	Receiving water body monitoring station
A2	Receiving water body monitoring station with only flowrate data available
ASB	Analytical-solution-based
B	Boron
BAT-AEL	Best available techniques associated emission limit
BATs	Best available techniques
BREF	Best available techniques reference document
Cd	Cadmium
CN	Cyanide
CoC	Contaminant(s) of concern
COD	Chemical oxygen demand
D	Discharge monitoring station
D2	Discharge monitoring station with no upstream receiving water body monitoring station available
D3	Discharge monitoring station with effluent discharged to another facility rather than a receiving water body
D4	Discharge monitoring station that is planned as a receiving water body monitoring station, however since receiving water body could not be found, the samples were taken from a discharge canal
DQ	Discharge quota
EQS	Environmental quality standard
E-ToD	Empirical relations based on a fundamental theory of dispersion
EU	European Union
IED	Industrial Emissions Directive
IPPC	Integrated Pollution Prevention and Control
L	Length
M	Mass

MS	Monitoring station
NH ₄ -N	Ammonium nitrogen
Ni	Nickel
OIZ	Organized industrial zone
PC	Process contribution
RWB	Receiving water body
T	Time
TDS	Total dissolved solids
Ti	Titanium
TKN	Total Kjeldahl Nitrogen
TNPM	Total number of periods monitored
TOC	Total organic carbon
TP	Total phosphorus
US	The United States
WFD	Water Framework Directive
WQM	Water quality monitoring
WWTP	Wastewater treatment plant

LIST OF SYMBOLS

SYMBOLS

$\varepsilon_{K,z}$	Local vertical shear dispersion coefficient [L^2/T]
κ	von Karman coefficient
$\varepsilon_y(y)$	Local transverse dispersion coefficient [L^2/T]
$\bar{v}_z(y)$	Local depth averaged velocity [L/T]
ψ	Revision coefficient
β	Channel shape parameter
$\varnothing$	Pipe diameter [L]
A	Mean cross sectional area [L^2]
C	Concentration [M/L^3]
C_0	Concentration at the point of discharge in the receiving water body [M/L^3]
C_{Chezy}	Chezy constant
$C_{dissolved}$	Dissolved concentration of the CoC [M/L^3]
C_{DL}	Discharge limit concentration of the CoC [M/L^3]
C_{total}	Total concentration of the CoC [M/L^3]
C_{TSS}	Concentration of total suspended solids [M/L^3]
C_w	Discharge concentration of the contaminant of concern (CoC) [M/L^3]
d	Mean depth [L]
D	Molecular diffusion coefficient [L^2/T]
Da^I	Advective Damkohler number
Da^{II}	Dispersive Damkohler number
$d_{i,j}$	
d_i &	Local depth [L]
$d(y)$	
DQ	Discharge quota (M/T)
DQU	Discharge quota used (%)

D_x	Longitudinal dispersion coefficient [L^2/T]
D_x	Longitudinal dispersion coefficient [L^2/T]
D_y	Transverse dispersion coefficient [L^2/T]
D_y	Transverse dispersion coefficient [L^2/T]
EQS & C_{EQS}	Environmental quality standard value for the CoC [M/L^3]
E_y	Transverse turbulent diffusion coefficient [L^2/T]
f^*	Darcy-Weisbach friction factor
F_1 & F_2	Rozovskii's dimensionless functions
J_{adv}	Advective flux [$M/T/L^2$]
J_{dif}	Diffusive flux [$M/T/L^2$]
k	First-order biodegradation constant
k'	Bed roughness
K_p	Partition coefficient
K_y	Transverse shear dispersion coefficient [L^2/T]
K_z	Vertical shear dispersion coefficient [L^2/T]
L_y	Transverse characteristic mixing distance [L]
$L_{y,ASB}$	Analytical-solution-based transverse characteristic mixing distance [L]
$L_{y,E-ToD}$	Empirical transverse characteristic mixing distance based on a theory of dispersion [L]
$L_z,$	
$L_{z,1}$ & $L_{z,2}$	Vertical characteristic mixing distance [L]
n	Number of imaginary sources
PC	Process contribution (%)
Pe	Peclet number
Pe	Peclet number
Q	Flowrate [L^3/T]
Q_{90}	Statistically, the flowrate value that is exceeded in 90% of the recorded cases for a given RWB
q_i	Second local factor for flowrate estimation [L^2/T]

Q_r	Receiving water body (RWB) flowrate [L^3/T]
Q_w	Discharge flowrate [L^3/T]
R	Reaction/transformation term [$M/L^3/T$]
r_c	Radius of curvature [L]
R_C	Ratios of CoC concentrations (C_{DL}/C_w)
R_{Ly}	Ratios of transverse characteristic mixing distances ($L_{y,E-ToD}/L_{y,ASB}$)
S	Channel slope
t	Time elapsed [T]
u^*	Shear velocity [L/T]
$U_{i,j}$	First local factor for flowrate estimation [L^2/T]
u_r	Radial velocity [L/T]
v	Mean velocity [L/T]
v_j &	Local velocity [L/T]
v_i	
W	Mass loading [M/T]
w	Mean width [L]
W_{DL}	Discharge limit for the CoC as mass loading [M/T]
w_i	Local width [L]
W_r	Upstream mass loading of the CoC in the receiving water body [M/T]
W_w	Mass loading of the CoC in the discharge [M/T]
x	Distance in longitudinal direction (direction of flow) [L]
y	Distance in transverse (lateral or horizontal) direction (along the width) [L]
z	Distance in vertical direction (along the depth) [L]

CHAPTER 1

INTRODUCTION

Around the world, water quality in surface water resources has become a significant issue with the rapid advancement of industries and urban areas. This is because of the excessive amount of water utilized by intense anthropogenic activities. This water, after being used either for household or industrial purposes will have some -even if not toxic- undesirable chemical substances and will generally be disposed of to any available receiving water body. Since many of such discharges to receiving water bodies will potentially increase the natural concentrations of these substances in the receiving water body, they are likely to pose environmental risks for both human health and the well-being of the aquatic life.

Legislations have been put into force by many countries to prevent such risks. As one noteworthy example, European Commission brought the Water Framework Directive (WFD) into force in 2000. With the enforcement of this directive, potentially harmful chemical substances for surface water bodies were named as contaminants of concern (CoC) and environmental quality standards (EQSs) which indicate maximum allowable concentrations for these substances in various types of water bodies were set.

In order for any government to be able to comply with these EQSs in river basins, they need to monitor water quality parameters at different points throughout the rivers, and control both diffuse and point sources of pollution. Among these two, identification and prevention of point source pollution is more straightforward.

A well-known and widely-accepted principle in the prevention of point source pollution is the “polluter pays principle” which is also adopted in WFD. According to it, dischargers are held responsible for the damage their discharges have on the

receiving water body and they are expected to minimize this damage to the level achievable by the best-available-techniques (BATs). BATs can be briefly defined as the state-of-the-art techniques which are both technologically available and economically feasible.

The minimum discharge concentrations attainable via BATs may still not be sufficient. CoC concentrations in the receiving water body need to be evaluated and compared with the EQSs. To know about the CoC concentrations around the point of discharge to a natural stream, one needs to know about the characteristics of mixing there.

Mixing of substances in rivers is a complex phenomenon which is a result of different transport processes acting upon them and influenced significantly by hydro-geometric conditions prevailing at the discharge point. Nevertheless, these processes have to be modeled with certain accuracy in order to decide whether dilution by mixing will reduce the concentration of any CoC below its EQS that would make the discharge permissible for that particular substance. And if not, the discharger must be forced to reduce CoC concentrations that cause exceedance of EQSs in the receiving water body.

The extent of reduction that would be needed in such conditions is determined according to the size of the mixing zone. Mixing zone is the region in the vicinity of a discharge, bounds of which is determined by the degree of mixing of that discharge. Thus, it can be said that the mixing zone is confined by the distance in the direction of the river flow, where a particular discharge becomes completely mixed across the depth and the cross-section of the river.

In order to estimate the bounds of this mixing zone, previously mentioned mass transport models are indeed utilized. However, many theoretical models that describe transport processes in rivers require long-term monitoring data which is still lacking for many countries who also aim to achieve good surface water status in their river basins.

The aim of this study is to develop a relatively simple and less data-driven approach for establishing concentration limits for potential point source discharges and demonstrate the application of the proposed approach with a case study on Tersakan sub-basin of Yeşilırmak river basin. To do so, the text starts with a literature survey regarding the main concepts of point source pollution control in natural river systems followed by an elaboration on the concept of mixing zone, and then mention in general terms about discharge limit establishment methods before going into further detail about the site of the case study, Tersakan sub-basin, industrial sectors present, receiving water body and discharge monitoring studies at the site, and the preparation and presentation of the relevant portion of the data collected. After introducing the study site and laying out the fundamental parameters, a detailed explanation of the novel approach proposed in this study for the estimation of discharge limits is given. Lastly, the approach developed will be implemented for the suitable discharge cases within Tersakan sub-basin and the results will be discussed thoroughly.

CHAPTER 2

LITERATURE SURVEY

This chapter includes a detailed review of literature in the scope of point source pollution control in riverine environments. The survey begins with the definitions of important concepts related to river water quality and continues with a brief summary about the fundamental aspects of river water quality monitoring which is a prerequisite for discharge limit estimation. The rest of the literature survey covers historical development of river water quality legislation in the US, the EU and Turkey and the current status and techniques used for point source pollution control.

2.1. Concepts of River Water Quality

Although it seems abundant in the Earth relatively to others, *water* is perhaps the most important natural resource of all. It is vital for human life as well as the existence of all organisms [1]–[3].

On the Earth, 96.5% of water is in the sea [3], and this sea water is transported back to land by the *hydrological cycle*. In this cycle, water evaporates from the sea and precipitates back over the sea and the land. On the land, some of it is used up by the plants and transpired to atmosphere, another portion percolates through the soil and gets stored in aquifers, the rest of it flows into rivers by surface runoff and turns back to the sea either by streamflow or evaporation [2]. For a more detailed presentation of distribution of Earth's water resources see Table 2.1.

Table 2.1. *Distribution of Earth's water resources* [4], [5]

Region	Volume (10^3 km^3)	% of total
Oceans	1,350,000	94.12
Groundwater	60,000	4.18
Ice	24,000	1.67
Lakes	230	0.016

Table 2.1. *Distribution of Earth's water resources* [4], [5] (cont'd)

Region	Volume (10³ km³)	% of total
Soil moisture	82	0.006
Atmosphere	14	0.001
Rivers	1	

In this greater picture of water cycle, only *freshwater* which is located on the land, can be used for human activity [2], making it the most relevant portion of *water resources* for societies. People necessitate freshwater for domestic purposes (drinking, washing, cooking), to produce animals and plants for various purposes, in industrial processes, and for recreation [2], [4].

Freshwater can be obtained from three sources, namely; *surface waters* which consists of rivers, lakes and reservoirs [4], [6]; ground water and rainfall [2]. The total of freshwater from these sources, nevertheless, comprises only 0.7% of the Earth's overall water reserves [3].

This constitutes actually a small volume of water considering the increasing demand for water. Between the 1950s and the 1990s, global water use has tripled [3]. And this is not only due to the increase of human population, the advancement of industry and evolving needs in materially prosperous societies also create a high pressure on water resources [3]. Therefore *sustainable development* must be pursued, which indicates that current needs ought to be met, without compromising the needs of the future generations [3]. Freshwater should be considered as a natural resource to be protected [7]–[9] for the sake of sustaining both the health of the economy and the environment [7]. Furthermore, sustainable development has the following more concrete implications for freshwater resources [3]:

- Secure supplies of safe drinking water in sufficient amount
- Additional supplies of water with sufficient quality and quantity for utilization in other economic activities such as industry and agriculture

- Water resources that enable safeguarding and sustaining good ecological state and functioning of the aquatic environment
- Management of water resources to prevent or reduce the adverse effects of floods and droughts

Among these, historically most attention has been given to *rivers* or *natural streams*, as a result of their higher visibility and ability of transporting water. Due to this ability, rivers seemed as good means of both water supply and waste disposal [4], [6].

However, the utilization of natural streams for both of these purposes, made them a cause of disease transmission as well. Such disturbances, caused by more readily identified, discrete and localized sources, are called as *point source pollution* which arise from industrial discharges and municipal sewage outfalls, as well as specific events such as chemical spills [2], [6], [10].

Non-point or diffuse source pollution on the other hand, results from the collection of pollutants distributed through a large area and therefore, the exact sources are not easily detectable [2], [6]. This area which drains and collects all types of water (and pollution) to the river, is called the *watershed*, *catchment* or *basin* of that river [4], [6]. In non-point source pollution, pollutants can be transported into rivers by surface runoff, groundwater inflow or atmospheric transport. Two most important examples of non-point source pollution is agricultural fertilizer and pesticides carried from fields and automobile emissions from urban drainage [2], [6].

In recent years, it was internationally recognized that many of the previous environmental problems encountered in “the developed countries” have arisen from the lack of appreciation of the pollution caused by anthropogenic activities. Besides, advancements like the ability of detecting trace substances in water bodies and their health effects, and our expanded knowledge on food chains and complex biochemical and ecological reactions have also increased public’s attention and awareness about environmental problems related to water resources [3].

In light of such evolvments, the protection of freshwater resources from all types of pollution has become a much significant issue. The greatest progress in this field has been observed in the US and the European Union. In the US, efforts to achieve acceptable freshwater quality have been maintained since the late 1940s and has been more systematized since the early 1970s [11].

Though, throughout the European Union (EU) a common understanding about this matter cannot be achieved till the late 1990s. Directive 96/61/EC, or the Integrated Pollution Prevention and Control (IPPC) Directive was implemented in 1996 and created a general framework for preventing or reducing pollution caused by industrial activities. Although at the time, the specific implications of both concepts for various conditions were not exactly known, with this directive, the distinction between environmental quality standards and emission limit values have been clearly stated. *Environmental quality standards (EQSs)* are requirements (such as concentration limits for certain substances) that should be met in any environment, say river water, in order to achieve acceptable status, and are based on toxicity studies. *Emission limit values* are imperatives of the discharges, which are imposed by the authorities in order to protect the environment from excessive pollution loads. The EU Member States have been obliged to take all measures in order to prevent industrial pollution, particularly by the application of *best available techniques (BATs)*. These are the techniques that are the most effective in protecting the environment as a whole, and are both technologically accessible and economically feasible. According to the IPPC directive, the BATs form the basis for an emission limit value, yet they can be overridden by stricter values, if the implementation of BATs would not be sufficient to achieve environmental quality standards in the receiving body [12].

After the implementation of the IPPC Directive, in 2000, *the Water Framework Directive* (WFD) came into action. The WFD has clearly defined the distinction and relationship between emission limit values and environmental quality standards, and introduced “the combined approach” where the importance of the water quality in a receiving water body after a discharge in permitting discharges has been emphasized.

For the establishment of environmental quality standards, a list of *priority substances* was provided which signifies that the EQS values for these substances can never be exceeded in any water body. The WFD has also imposed the Member States to focus on river basins as a whole rather than considering individual points on a stream and to create river basin management plans. With the introduction of river basin management plans, *river basin specific pollutants* became also of concern, these are substances other than the priority hazardous substances that are being discharged in significant quantities into specific rivers [13].

Finally in 2008, the European Commission implemented the EQS Directive, where EQS values for the priority hazardous substances were established. In addition, clarifications about more complex, detailed and technical issues related with the implementation of the WFD including the establishment of EQS and emission limit values, mixing zones and transboundary pollution were provided [14].

2.2. River Water Quality Monitoring

Water quality monitoring (WQM) for rivers is a completely separate area of expertise. However, some basic aspects of river WQM is summarized in this section since high quality data is very crucial in order to achieve sustainable good water status throughout rivers. One branch of the efforts to maintain good water status in natural streams is to control point source pollution, which is the main focus of this study. A prerequisite also to properly accomplish this, is to have the water quality data to understand the conditions at any discharge point and to take decisions accordingly. After all, the foundation of all work that is related to water quality management, including this one, is water quality monitoring [15].

In many parts of the developed world, monitoring of river water quality has been implemented as early as the beginning of the 1970's [16]. However, most of these efforts were not systematically sustained throughout the years or performed under networks that are designed according to only a criteria of convenience, without a consistent and rational strategy [17].

A WQM network or program is a structure that involves the different aspects of a long-term plan for the water quality monitoring for a given water body (watershed, river, lake etc.). This structure includes the objectives, sampling sites, water quality parameters, sampling frequencies, duration of sampling, need of human, technical and economic resources, required field and laboratory work, approaches of data preparation and dissemination, and methods of data analysis and interpretation [15], [16], [18], [19].

The efficiency and success of a WQM program has become more important with stricter environmental legislations. A good example can be seen in the Water Framework Directive (WFD) that is put into force by the European Community [13]. This document that includes a special article regard WQM, obliges all Member States to establish programs of WQM in order to have a comprehensive and coherent overview of water status in all river basin districts [13]. A guidance document on monitoring under the WFD has also been published later as a common implementation strategy [20]. In it, tangible suggestions related to all elements of a WQM program is provided.

It is known that delineation of objectives is the first step during the design of a WQM program and thus has a key role [16], [19]. A WQM program is prone to failure if its objectives are specified improperly and ambiguously [16]. Guidance from the European Community includes the below objectives for WQM programs [13], [17], [20]:

- To help identify status of water for the given water body(ies)
- To aid risk assessment practices
- To assist in the follow-up of both natural and human-induced long-term changes
- To asses compliance with legislative aims and standards
- To learn about the efficacy of restorative measures
- To evaluate the effects of an accidental pollution

The number and placement of sampling sites in a WQM program is a crucial design factor to be considered. Formerly, many governmental agencies selected location for the monitoring stations in a WQM program by a sole criteria of convenience, such that it is near a bridge [17]. However, a more reasonable principle coined by Sanders et al. to decide the number and locations of monitoring stations in a river basin WQM program is that in the end, the network should generate information representative of each reach of the stream and of the river system's overall condition [16]. So as to apply this principle, many WQM networks are designed by dividing the sampling locations into two groups, namely, macrolocations and microlocations. Macrolocations signify the reaches that are to be monitored in a river basin, microlocations are the actual sampling points, usually critical locations on a reach such as upstream of a particular discharge or near a water intake [17], [18].

For the optimization of and redesign of existing WQM networks both quantitative and qualitative approaches are employed. Quantitative methods include multivariate statistical analyses (such as principal component analysis, principal factor analysis, cluster analysis, and discriminant analysis); genetic algorithms, entropy methods, and multicriteria analysis [18]. As qualitative approaches, site representativeness, accessibility, and number of contributing tributaries are among others to consider [18].

Water quality parameters to be monitored as part of a WQM program are primarily based on the objectives of the WQM program [16], [17]. In many cases, a WQM would start with a higher number of water quality parameters and would decrease their number gradually by reassessment of network-wide risks and objectives. It is important to note that in order to provide a systematic and coordinated operation of the network and to able to obtain information regarding the general condition of any river system, a common list of water quality parameters should be monitored in each station of the network [16].

However, financial and technical constraints should also be taken into account without causing considerable loss of information that would result in failure to achieve the one

or more of the monitoring objectives [16]. Such constraints can be unignorable especially in developing countries [16]. Besides the financial benefit, it is also advisable to reduce the number of water quality parameters for more convenient analysis of the results (e.g. investigation of dependencies and correlations), saving both time and effort [17].

Temporal frequencies of WQM programs influence the sampling costs considerably. In this sense, during the design of such programs, the matter of sampling frequencies are considered with high scrutiny [16], [17]. If the temporal frequencies are too often, redundant data would be collected and thus unnecessary expenses would be created. Otherwise, infrequent sampling would result in omission of information that is essential for the objectives of any WQM program [16], [21].

As part of the initial attempts to monitor river water quality in the past, sampling intervals used to be infrequent due to being determined by technical and human resource capacity [17]. Along with the objectives of the particular WQM program, temporal frequencies are determined in accordance with the relative importance of stations in the network, and the expected variability of the water quality parameters in each station [17]. Nonetheless, for the systematic operation of the WQM program, common practice is to select a common frequency at least for each parameter throughout a WQM network [16].

Reasonable selection of temporal frequencies for WQM programs is considered as a statistical process [16]. Data for each water quality parameter in each sampling station have to be populated enough to ensure a mean within an acceptable confidence limit [17]. Various statistical methods for this purpose can be listed as “determination of statistical properties of water quality series, ratios of maximum flows, determination of confidence intervals for mean values, evaluation of sampling errors and their variance, or determination of required numbers of data for testing statistical hypothesis” [16].

The final large step of a WQM program is the analysis and interpretation of the data and thus, its transformation into desired information. Various techniques can be employed in order to generate information that is understandable for different stakeholders. Some examples are utilization of statistical tests and software to extract representative singular values from a large amount of data, application of spreadsheet software in order to generate plots, graphs, charts and tables, employment of geographic information systems (GIS) software to study spatial relations (land use, rainfall-runoff etc.), or usage of water quality modeling software to assess legislative conformity [15]. The main focus of this thesis falls under this final step, more specifically under the latest of the examples given in the previous sentence.

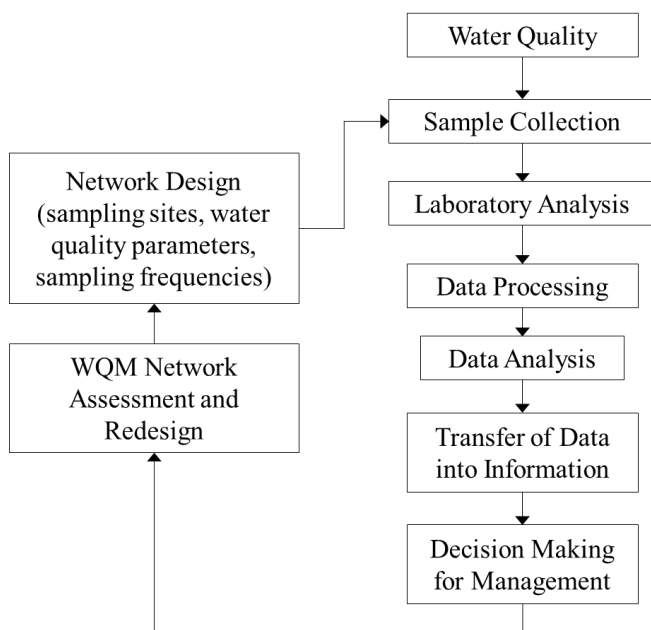


Figure 2.1. Water quality monitoring program stages [16]

As mentioned above, based upon the objectives of the WQM program, relevant data have to be generated from the data gathered by monitoring. Therefore the available data must be in such quality that it can generate required information. So as to

maximize the utility of the data, it should be subjugated to data management. Since the output of each step of a WQM program is the input of the next one (refer to Figure 2.1 for the representation of the steps of a WQM program), WQM programs need to be perceived as a whole with interdependent pieces where each of the pieces are equally significant. Hence, each component part of a WQM program have to be motivated by a common set of WQM objectives and have to be of high quality. Because problems, errors and inevitable uncertainties in each step would accumulate and could ruin the information that is generated at the end, which would imply the failure of the program as a whole and a serious economic loss [16].

In conclusion, today, when fresh water resources are depleted at a never before seen rate because of human conduct and therefore legislative obligations to monitor surface water quality become much pronounced, establishment of efficient WQM programs throughout each watershed in the world is both an urgent need and a challenge. Previous experience shows that definition of precise and tangible WQM objectives plays a key role in ensuring a successful WQM program. These objectives then should be abided while designing and operating each step of the WQM program with a sound notion of interdependency between each step, and thus a pursuit of standardized, high quality work at each step.

2.3. Point Source Pollution Control in Rivers

This section will go over the fundamental strategies taken to control point source pollution in rivers. Since some aspects of it have already been mentioned and detailed explanations will be provided in the upcoming chapters, this section aims to serve as a simple introduction to the subject.

The principle approach for the control of point source pollutions to rivers is through the application of permits by governing bodies. In many cases nowadays, this permitting procedure starts from the design and construction phase of any discharging facility and continues with periodic monitoring of the actual discharge and receiving body characteristics in order to detect any violation of legislative boundaries.

2.3.1. Discharge Standards or Best Available Techniques Associated Emission Limits (BAT-AELs)

Discharge standards, or best available techniques associated emission limits (BAT-AELs) are permitted limits for all contaminants of concern and reported as concentration (mass/volume) or pollution load (mass/time), that are set specifically in line with industrial limitations. Therefore BAT-AELs include different contaminants and limit values for different sectors.

The concept of BATs have been around for at least 40 years in terms of environmental legislation in the US [22]. However, the widespread adoption of the term across the European Union had not been realized till the late 1990s. In 1996 with the implementation of Directive 96/61/EC, or the Integrated Pollution Prevention and Control (IPPC) Directive, the European Communities have come to terms with the fact that commonly accepted standards to minimize the whole environmental impact of industrial activity were necessary. This directive has been amended several times in later years, namely three times in 2003 and once in 2006 [23]. In 2008 the previous amendments were integrated in a codified version of the directive [23]. Finally in 2010, the IPPC Directive and six other related directives were recast as Directive 2010/75/EU, or the Industrial Emissions Directive (IED) [24].

Best available techniques indicate the state-of-the art processes and their methods of application that are practically suitable for the prevention or if not possible and for more often cases reduction of pollution, or more comprehensively the overall environmental impact caused by any activity. A word-by-word analysis of the concept is given as follows in the European Commission's Directives [12], [23], [24]:

- “techniques” involve all steps a technology can pass through during an activity including design, building, assembly, installation, operation, maintenance and decommissioning

- “available” counts both for technical and economic accessibility and implies the techniques that are sufficiently developed that can be implemented in the relevant industrial sector considering its current conditions
- “best” means the most effective options for accomplishing high overall environmental performance (including air, water, and land emissions, waste generation, raw materials usage, energy efficiency, accident prevention, and site restoration upon closure [25])

Emission limit values for specific pollutants discharged as consequence of various processes in a sector to different media (air, water, or land) are given in best available techniques reference documents (BREFs) for the EU. Currently 32 BREFs that cover distinct industrial sectors are available. 14 of these documents have been reviewed and harmonized with the IED. 17 of them have previously prepared BREF documents, some being older than 15 years. Out of these 17, 4 have published drafts, soon to be accepted, for other 3 of them, review process have commenced, and the other 10 still await a review. Only one of the mentioned sectors have not yet had any kind of a BREF document, however work started for its preparation as well (see Figure 2.2) [26]. Table 2.2 provides more detailed information about each sector involved in the progress.

In Turkey, such discharge standards for water discharges to rivers, have been in force since the implementation of Water Pollution Control Regulation prepared by the former Ministry of Environment and Forestry (now called the Ministry of Environment and Urbanization) in 2004. The regulation is still enforced and has been amended 9 times so far, once each in 2008, 2010 and 2011, four times in 2012, and once each in 2016 and 2018. Tables 5 to 20 in its appendix include permissible values for discharges of several pollution parameters for specific industrial sectors [27].

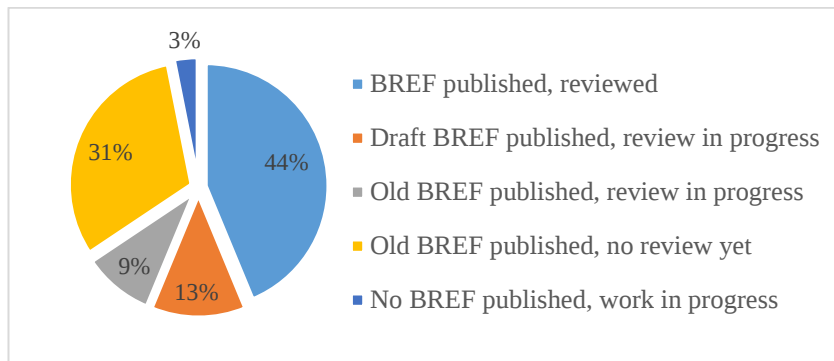


Figure 2.2. Chart that shows the current conditions of BREF documents prepared by the European Commission

It is important to note that BAT-AELs form merely a basis or a minimum requirement for discharge limit values. Governing bodies can put more stringent limitations if good water quality cannot be maintained at the receiving water body. Another point to consider is the rapid developments in technology which would result in changes for the BATs, therefore BAT-AELs are going to be evolved in time [12], [23], [24].

2.3.2. Environmental Quality Standards (EQSs)

EQSs are limit values for pollutants or groups of pollutants that cannot be exceeded in water, sediment or biota in order to protect human health and the environment. EQS values are derived from toxicological studies and therefore indicate the lines where serious health issues may arise due to short (acute) or long term (chronic) exposure to potentially harmful substances.

In the US, EQSs or specifically water quality standards have been included in environmental law since the late 1960s [22]. Such an early initial undertaking enabled the governing bodies in the US to build further upon in the later decades. Scientific research has also been fostered in order to meet the lack of knowledge about the health effects of various potentially hazardous substances [22].

Table 2.2. *Table of sectors covered in European Commission's BREF documents and their current status [26]*

No.	Sector Name	Sector Code	BREF published, reviewed	Draft BREF published, review in progress	Old BREF published, review in progress	Old BREF published, no review yet	No BREF published, work in progress
1	Ceramic Manufacturing Industry	CER				✓	
2	Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector	CWW	✓				
3	Common Waste Gas Treatment in the Chemical Sector	WGC					✓
4	Emissions from Storage	EFS				✓	
5	Energy Efficiency	ENE				✓	
6	Ferrous Metals Processing Industry	FMP		✓			
7	Food, Drink and Milk Industries	FDM		✓			
8	Industrial Cooling Systems	ICS				✓	
9	Intensive Rearing of Poultry or Pigs	IRPP	✓				
10	Iron and Steel Production	IS	✓				
11	Large Combustion Plants	LCP	✓				
12	Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers	LVIC-AAF				✓	
13	Large Volume Inorganic Chemicals – Solids and Others Industry	LVIC-S				✓	
14	Manufacture of Glass	GLS	✓				
15	Manufacture of Organic Fine Chemicals	OFC				✓	
16	Non-ferrous Metals Industries	NFM	✓				
17	Production of Cement, Lime and Magnesium Oxide	CLM	✓				
18	Production of Chlor-alkali	CAK	✓				
19	Production of Large Volume Organic Chemicals	LVOC	✓				
20	Production of Polymers	POL				✓	
21	Production of Pulp, Paper and Board	PP	✓				
22	Production of Speciality Inorganic Chemicals	SIC				✓	
23	Refining of Mineral Oil and Gas	REF	✓				
24	Slaughterhouses and Animals By-products Industries	SA			✓		
25	Smitheries and Foundries Industry	SF			✓		
26	Surface Treatment Of Metals and Plastics	STM				✓	

Table 2.2. *Table of sectors covered in European Commission's BREF documents and their current status [26] (cont'd)*

No.	Sector Name	Sector Code	BREF published, reviewed	Draft BREF published, review in progress	Old BREF published, review in progress	Old BREF published, no review yet	No BREF published, work in progress
	Surface Treatment Using Organic Solvents including						
27	Wood and Wood Products Preservation with Chemicals	STS		✓			
28	Tanning of Hides and Skins	TAN	✓				
29	Textiles Industry	TXT			✓		
30	Waste Incineration	WI		✓			
31	Waste Treatment	WT	✓				
32	Wood-based Panels Production	WBP	✓				
			14	4	3	10	1

However, for the European Union (EU) the term “environmental quality standards” was not a common concern until the implementation of the Directive 2000/60/EC or the Water Framework Directive (WFD). On this important legislative document, not only the concept was accepted and defined, but also goals were set to establish these limit values for contaminants that pose a high risk (i.e. priority substances) and to start implementing these limits in order to have good water status on all surface water across the EU. As a result of these goals, Directive 2008/105/EC or the Environmental Quality Standards (EQS) Directive has come into force in 2008. In it, the previously mentioned priority substances and the EQS values associated with them were established. Moreover, the EU Member States were encouraged to detect and set additional EQSs for river basin specific pollutants [14].

In Turkey, EQSs for surface water including rivers were established with close relevance to the European Commission’s EQS Directive as the Surface Water Quality Regulation was prepared by the Ministry of Agriculture and Forestry (then was called the Ministry of Forestry and Water Affairs) of the Republic of Turkey in 2012. It has been amended twice since its implementation (in 2015 and 2016) and sets the goal to attain the established EQS values by the end of 2019 (almost 7 years after the publication of the regulation) [28]. Because of the financial burdens and industrial priorities of the country, and the lack of a stable nationwide surface water quality monitoring system, the achievability of this goal is still unclear.

2.3.3. Discharge Limits and Mixing Zones

Discharge limits are restrictions established for contaminants of concern and reported as concentration (mass/volume) or pollution load (mass/time), which are determined primarily considering receiving water body conditions and are related both to sector based discharge standards and environmental quality standards (EQSs).

As can be understood from the previous two sections, EQSs apply to receiving water bodies and discharge standards or best available techniques associated emission levels (BAT-AELs) are valid for discharges. These two concepts, although coined to serve

the common goal to protect the environment has to somehow be reconciled, since EQS values for a given pollutant is often much less than what is achievable by the BATs.

The European Union (EU) in Directive 2000/60/EC or the Water Framework Directive (WFD) proposes a “combined approach” to reconcile the difference between EQSs and BAT-AELs, which indicates that these two values should be conceived as complementary, rather than contradictory [13].

The complementariness between the two are provided the employment of “mixing zones” and establishment of discharge limits. The clear definition and techniques of estimation for mixing zones were only available since the early 1990s in the US [29]. Although EQSs and industrial sector specific discharge standards were put in place and relevant research regarding mixing in surface waters was available for at least a decade, the delayed proposal of the concept of mixing zone was primarily due to the data required to run the models designed for their prediction. For the EU, however, it took almost two more decades to implement mixing zones into environmental legislation. The concept was introduced in Directive 2008/105/EC or the Environmental Quality Standards Directive in 2008 [14]. Complementary to the EQS Directive, “Technical guidelines for the identification of mixing zones” that explained methods and approaches for the identification of mixing zones was prepared by a working group under the European Commission in 2010 [30]. This guideline also provided a tool for the simple approximation of mixing zones, the Discharge Test Software, which is an MS Excel based computer program. In Turkey, “mixing zones” are briefly mentioned in the Surface Water Quality Regulation prepared by the Ministry of Agriculture and Forestry (then, the Ministry of Forestry and Water Affairs) promulgated in 2012, and no clear method for their estimation is referred to [28].

Obviously, in case where EQS value for a pollutant is stricter than BAT-AEL value for it, its concentration near the point of discharge in the receiving water body (i.e. river) will be greater than the EQS. A mixing zone is the relatively narrow portion of a water body, where a substance undergoes initial mixing. It is defined as the region

where the discharge is completely mixed in the vertical and the horizontal directions of the receiving water body. Longitudinal mixing is excluded because it is never actually completed. Regarding this conception of a mixing zone two questions regarding discharge concentrations occur:

1. Is the concentration at the end of the mixing zone in a receiving water body of any given pollutant with a specific discharge concentration, less than or equal to its EQS value?
2. What could the maximum discharge concentration of any given pollutant be in order to have its receiving water body concentration at the end of the mixing zone be less than or equal to its EQS value?

The former question can be useful while investigating the standing of a specific discharge, i.e. whether it is permissible or not. The latter one is more appropriate for the designation of discharge limits.

The extent of a mixing the receiving water body concentrations of a substance within and around that extent can be approximated by the use of environmental modeling. One of many examples (QUAL2K, CORMIX, Plumes etc.) used with this purpose is the Discharge Test Software developed by a team assigned by the European Commission (EC) which will be further investigated in the following section.

This study also proposes a new approach for the identification of mixing zones and relevant discharge limits. Fourth chapter of this text called “A Novel Approach for Discharge Limit Estimation” is dedicated entirely to this subject. Further general information about river mixing and mixing zone approximation will be provided there.

2.3.4. European Commission’s Tiered Approach

“Technical guidelines for the identification of mixing zones” prepared complementary to Directive 2008/105/EC, or the Environmental Quality Standards Directive, suggests an approach comprised of five stages (Tiers 0 to 4), in order to enable each discharge point to be investigated with a level of scrutiny that is only

necessary [14], [30]. In this section, these stages will be summarized with a specific focus on discharges to rivers.

In *Tier 0* the presence of the contaminant of concern (CoC) is ensured. If the concentration of the CoC is zero or less than the EQS value, then more detailed analysis is unnecessary, periodic monitoring of the CoC is sufficient.

Else, *Tier 1* is valid. This stage is where it is decided for CoCs with concentrations exceeding their EQS values whether or not mixing zone estimation would be necessary. A parameter called “process contribution” which is a measure of the CoCs’ concentrations in case of complete mixing, is utilized to make such determination. Process contribution is reported as %EQS and if it is under below certain values (see Table 2.3), than it indicates that more detailed investigation is not necessary periodic monitoring is sufficient.

$$PC = \frac{C_w Q_w}{(Q_r + Q_w) EQS} * 100 \quad (1)$$

where C_w is the discharge concentration of the CoC [M/L³], EQS is the environmental quality standard value for the CoC [M/L³], Q_w is the discharge flowrate [L³/T] and Q_r is the river flowrate [L³/T].

Table 2.3. Maximum permissible process condition values for rivers [30]

River types	Net flowrate (Q_{90}^1 flowrate) [m ³ /s]	Acceptable concentration increase after complete mixing as %EQS (suggested values)
Small	≤ 100	4
Medium	100 < flowrate ≤ 300	1
Large	> 300	0,5

¹ Statistically, the flowrate value that is exceeded in 90% of the recorded cases for a given receiving water body.

Else, either necessary precautions are taken or *Tier 2* is proceeded. This is the first stage in the approach that the concept of mixing zone is employed. In this stage the extent of the mixing and the CoC concentrations in and around it is approximated by simple models such as the Discharge Test software developed by the European

Commission. If this mixing zone seems to be clearly acceptable, then further investigation is not needed and periodic monitoring is sufficient.

Else, if the mixing zone poses a doubtless violation, authorities have to take immediate action to reduce the size and the effect of the mixing zone. Or else, if no explicit conclusion can be made from the results of the simple approximation model, then either Tier 3 or Tier 4 is proceeded.

Tier 3 is appealed to in cases where Tiers 0 to 2 are not sufficient to reach a clear conclusion about the acceptability of a discharge. In this stage, more advanced modeling techniques that are appropriate for a specific discharge case are employed to identify and investigate the mixing zone. For instance, if a one-dimensional, steady-state model was utilized in Tier 2, a more advanced option for Tier 3 would be a three-dimensional and non-steady state model. If an individual discharge is obliged to be investigated under Tier 3, this does not necessarily imply that discharge is likely to be unacceptable. It only indicates that the previous steps do not generate a satisfactorily clear decision. In order for Tier 3 to meet its objective, relevant modeling procedure should take the following into account:

- Spatial (three-dimensional) and temporal breadth of EQS exceedance zones (including statistical variability)
- Nature and size of the receiving water body (changes in hydrodynamic characteristics and chemical and physico-chemical quality)
- Location of the boundaries of the water body
- Concentration distribution and statistics within the EQS exceedance zone
- Distribution of receptors in the receiving water body (notably ones in the EQS exceedance zone and in sensitive areas and protection zones)
- Sensitivity of receptors to the CoC
- Expected effects in the EQS exceedance zone

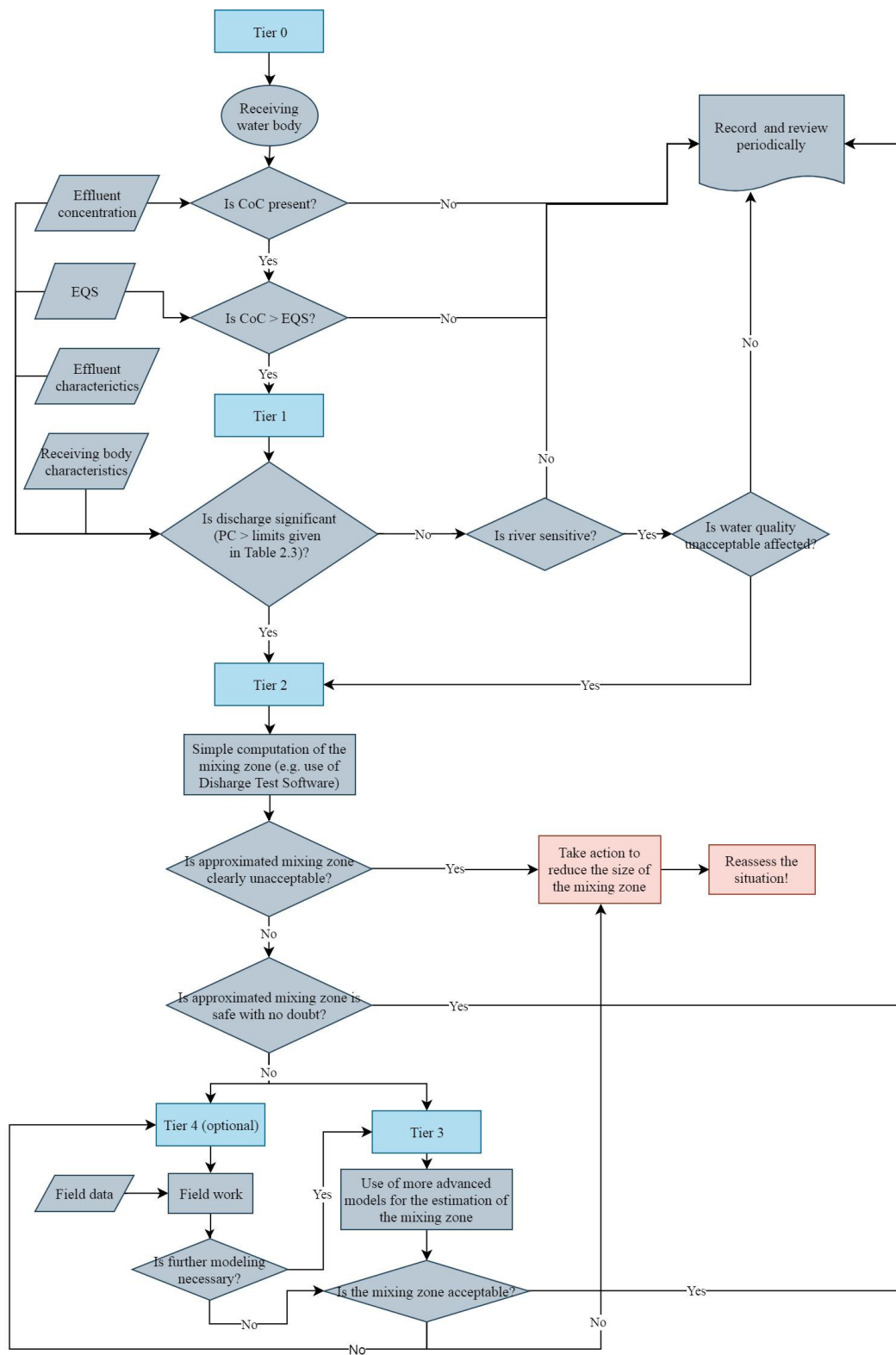


Figure 2.3. A summary diagram for all steps of the Tiered Approach

- The significance of these expected effects with regards to the ecological and chemical goals set in the watershed management plans (if any exists)

There are three possible outcomes from Tier 3. The discharge is either acceptable and no further effort except periodic monitoring is necessary, or the discharge seems unacceptable and one of proceeding into Tier 4 for further investigation regarding the discharge area or taking precautions required to reduce the size of the mixing zone has to be selected.

Tier 4 is an optional stage which can be referred to after either one of the mixing zone approximation stages (Tiers 2 and/or 3) where any kind of information about the discharge site including both discharge and receiving water body characteristics does not seem to be sufficient. So, Tier 4 involves the collection of missing or inadequate data to rule out the obscurities that prevent a final decision concerning the acceptability of the mixing zone.

2.3.5. European Commission's Discharge Limit Software

Directive 2008/105/EC, or the Environmental Quality Standards Directive allows Member States to identify mixing zones for all point source discharges and has prepared the “Technical Guidelines for the Identification of Mixing Zones” to delineate principles related. As an appendix to this document, the Discharge Test software has also been distributed. This is a software that utilizes a rather simple environmental model and therefore is the alternative suggested by the European Commission for discharge compliance investigations under Tier 2 of the Tiered Approach.

The Discharge Test software is programmed as an MS Excel Workbook and it was first developed for fresh water bodies and later has been adapted for other environments as well. Table 2.4 provides the details about each worksheet included in the software. Since it is founded upon simple solutions of Fischer's mixing equations [31], [32], it does not require an exhaustive amount of data. The data requirement of the software can be summarized as below:

- *Discharge data*

- *Discharge flowrate* (Q_w , L³/T)
- *Concentration of the contaminant of concern (CoC)* (C_w , M/L³)
- *Pipe diameter* (ϕ , L, if available, used to determine discharge flow speed, if information is not available, speed can be assumed as 2 m/s symbolically)
- *Discharged substance*

It is selected from a list. New entries can be added to list if the substance is not already on it, however special attention must be paid for some priority pollutants such as heavy metals. Since their EQS values are given on the list as dissolved, yet their discharge concentrations are measured as total. In such cases, because the difference between these values are primarily caused by particle adsorption, the following formula can be used for the conversion:

$$C_{total} = \frac{C_{dissolved} + K_p \frac{C_{TSS}}{10^6} C_{dissolved}}{10^6} \quad (2)$$

K_p : partition coefficient

C_{total} : Total concentration of CoC

$C_{dissolved}$: Concentration of dissolved CoC

C_{TSS} : Concentration of total suspended solids

- *Water body data*

- *Water type* (River/lake/canal/ditch or small canal)
- *Average flowrate* (L³/T, a flowrate that can statistically represent the water body is selected, such as Q_{90} , which is the flowrate that 90% of the measured flowrate values keep above and represents the low flow condition, that can be used as part of a conservative approach in mixing zone identification)
- *Dimensions of the water body* (depth and width, L)

- *Upstream concentration of the CoC* (M/L^3 , background concentration of the CoC can also be taken)
- *Bed roughness*

Provided that all the above data are available, the software can be run under three different methods which indicates that the software is a flexible tool that enables the user to investigate many options or scenarios by altering various parameters:

1. The actual sizes of the mixing zone bounded by the annual average and maximum allowable EQS values
2. Consequences (EQS exceedances) of a discharge at predefined maximum longitudinal downstream distances where EQS exceedance is allowable (or extent of mixing zones)

Below are the values given by the EC for these maximum allowable distances (which do not apply if water is abstracted for human use) [32]:

For annual average EQS = $\text{MIN}(10 \times \text{width of water body}; 1000 \text{ m})$

For maximum allowable EQS = $\text{MIN}(0.25 \times \text{width of water body}; 25 \text{ m})$

3. Free selection of mixing zone dimensions

Table 2.4. *Details about each worksheet included in the Discharge Test software which is programmed as an MS Excel Workbook*

Worksheet	Aim/Function
1) Discharge Test	Water body and discharge data is entered. Results of the general assessment is shown.
2) Calculation of Mixing	Detailed information about the dimensions of the mixing zone and results at the level of the receiving water body are shown.
3) Standards	Substance list and related EQS values
4) Legend	List of utilized parameters
5) Mixing in Tidal Situation	Calculations regarding tidal conditions

In the final part of this section, a very brief introduction to the the mathematical approach adopted in software will be made. As mentioned earlier in the section, the software benefits from Fischer's mixing equations [31], [32], and specifically their rather simple analytical solutions under steady-state and continuous discharge conditions. The most general form of such solutions is given as [32]:

$$C(x, y) = \frac{W}{d v \sqrt{\pi D_y \frac{x}{v}}} \sum_{n=-\infty}^{n=\infty} \exp \left[-\frac{(y - 2n w)^2}{4 D_y \frac{x}{v}} \right] \quad (3)$$

where $C(x, y)$ is the concentration of the CoC at x m in the longitudinal and y m in the transverse direction apart from the point of discharge $[M/L^3]$, W is the discharge loading of the CoC $[M/T]$, d is the depth $[L]$, w is the width $[L]$, v is the velocity of the water body $[L/T]$, n is the number of imaginary sources, and D_y is the transverse dispersion coefficient $[L^2/T]$.

$$D_y = \text{MAX} \left(v d \frac{\sqrt{10}}{C_{Chezy}}; 0.001 \right) \quad (4)$$

where C_{Chezy} is the Chezy constant and the dimension of 0.001 is m^2/s (typical values of D_y for rivers are in the range of 0.01-0.05 m^2/s).

$$C_{Chezy} = 18 \log \left(\frac{12 w d / w + 2 d}{k'} \right) \quad (5)$$

where k' is the bed roughness (dimensionless variable, its value changes from 0.05 for rivers to 0.1 for canals and lakes).

2.3.6. Precautions to Reduce the Mixing Zone

From the previous sections, it should be evident that, although it provides a compromise between best available techniques associated emission levels (BAT-AELs), or industrial sector specific discharge standards, and environmental quality

standards (EQSs), the utilization of mixing zones does not ensure all discharges to be permissible. Some discharges will be unacceptable and their mixing zones will need reduction for the protection of the receiving water body.

After all, the aims of the methodology developed by the European Commission (EC) for the identification of mixing zones are to protect water quality, limit negative impacts and prevent sediment pollution within any mixing zone.

To achieve these goals, below precautions can be taken to reduce the extent of the mixing zone of any unsanctionable discharge:

- *Up-to-date follow-up and application of the best available techniques (BATs):* The discharger should make efforts to keep up with, develop and implement new technologies included in or beyond the content of the BAT references documents (BREFs) prepared by the EC.
- It could be demanded from the discharger *to reduce discharge load, flux and/or concentration with time* according to receiving water body characteristics such as flowrate, ambient quality, temporary existence of a sensitive receptor etc.
- *Other emissions could be managed* in order to reduce upstream/background concentrations.
- *Review of the outfall layout to change initial mixing conditions* (location, plan, vertical alignment, design, number and orientation of the outlets, effluent velocity etc.; this would not alter the effect of the discharge on further downstream background concentration)
- *Backwards mixing or receiving water flowrate management to provide a higher receiving water body flowrate* (thus, more dilution)

The review of the literature given in this chapter includes some important findings that form the fundamental motivations for the development of a novel approach for EQS-based discharge limit estimation to be used in Turkey, and especially in the study site,

which is Tersakan sub-basin of Yeşilırmak river. The lack of a sustainable and integrated water quality monitoring network that could generate receiving water body and discharge data, creates an important challenge for the case at Tersakan. The European Union's Discharge Test software that is covered in the review, is an approach alternative to more advanced modeling tools (such as PLUMES or CORMIX) that can be used for this purpose under more data-scarce conditions. However, this tool is designed as a one-size-fits-all approach and it has minimal ability to adapt to different mixing conditions prevailing in different discharge points. The novel approach that is developed in this study (see Chapter 4), has more flexibility and incorporates various modifications that covers diverse conditions that can exist at particular discharge points.

The details about the actual conditions prevailing at the receiving water body and discharge monitoring stations within Tersakan sub-basin are presented in the next chapter.

CHAPTER 3

MATERIALS AND METHODS

In this chapter a detailed description of the study area, where the water quality and hydro-geometric data were collected, is introduced. Also the methods employed to process and prepare the site-specific data needed for the application in the discharge limit establishment tool that is developed during this study (see Chapter 4) are explained.

3.1. Information about the Study Site

As part of a more extensive research project funded by TÜBİTAK (Project No: 115Y013) regarding the control of point and diffuse source pollution in Yeşilırmak Basin in Turkey, data about receiving water body and point source discharge characteristics have been collected 8 times between August 2016 and January 2018 throughout the whole watershed.

A particularly significant tributary of Yeşilırmak Basin is Tersakan Creek due to being exposed relatively intense amounts of agricultural and industrial pollution loads. Therefore among many other sub-basins in Yeşilırmak Basin Tersakan sub-basin has been selected for environmental quality standards (EQS) based discharge limit establishment applications.

Tersakan Creek has a length of 91.4 km and has a catchment area of 2,684 km². It springs from Ladik Lake and flows in north-west direction, until it reaches Havza. Then, it turns towards south and arrives at Suluova. Later, it combines with Salhan Creek to continue its flow in south-east direction. Finally, it combines with Yeşilırmak River near the north of Amasya. Because of this flow course it is named as Tersakan (Reverse-flowed, since it flows from the sea to the land). Important tributaries that

feed Tersakan Creek are Demiröz Creek on its east and Çayırözü Creek on its north-west (see Figure 3.1 on p. 36).

Major industrial facilities that generate wastewater and are located within Tersakan sub-basin are given in Table 3.1. According to this table, the predominant sectors in the area are production of milled grains and vegetable products. Other sectors present include ready-to-use animal feed production, slaughterhouses and meat production, sugar production and mining. Eleven among these facilities were included in the monitoring efforts and have been visited.

Table 3.1. *Major industries located within Tersakan Creek sub-basin*

No	Monitoring	Name of the Facility	NACE	North Coord.	East Coord.
1	✓	Akçansa Cement Industries	23-51	40,934776	35,885779
2	✓	Aktan Food Industries	10-61	40,884275	35,635308
3	✓	Amasya Sugar Factory	10-81	40,832484	35,644532
4	✓	Aydınöğlü Flour and Food Industries	10-61	40,980545	35,688559
5	✓	Beşgöz Araboğulları Flour Industries	10-61	40,917721	35,648131
6	✓	Doğa Su Food Industries	11-07	40,893082	36,057595
7	✓	Et-Bir Slaughterhouse	10-13	40,823054	35,636581
8	-	Gülşim Flour and Semolina Industries	10-89	40,828350	35,632949
9	✓	Gürmin Energy and Mining	05-20	40,881773	35,632456
10	-	Kanoğlu Flour, Food And Agriculture Industries	10-61	41,002209	35,822660
11	✓	Kozlu Food Production Industries	10-91	40,848721	35,630486
12	-	Nur Flour Industries	10-61	40,968378	35,669228
13	✓	Otat Food Industries	10-50	40,97504	35,687155
14	✓	Temiz Meat Products Facility	10-11	40,997111	35,662839
15	-	Yeni Teşvikiye Feed Industries	10-91	40,943111	35,656215

Two active wastewater treatment plants (WWTPs) within the sub-basin were included in the monitoring efforts, namely Havza Municipal WWTP and Merzifon Organized Industrial Zone (OIZ) WWTP.

To see all wet and dry streams, receiving water body and discharge monitoring stations on a map refer to Figure 3.1. Detailed information regarding monitoring visits to all of the receiving water body and discharge monitoring stations are given in Table 3.2. According to Table 3.2, there are 14 receiving water body and 12 discharge, which indicates a total of 26 monitoring stations within Tersakan sub-basin that monitoring data could at least once be collected.

As can be seen from Table 3.2, not all of the visited monitoring stations yielded data during every monitoring season (Aug-2016, Oct-2016, Feb-2017, Apr-2017, Jun-2017, Aug-2017, Nov-2017, Jan-2018). As a result, for the identification of receiving water body-discharge monitoring station couples to be used in EQS-based discharge limit establishment application, the monitoring stations that have yielded at least one set of monitoring data and have not been by any reason cancelled are schematized in Figure 3.2.

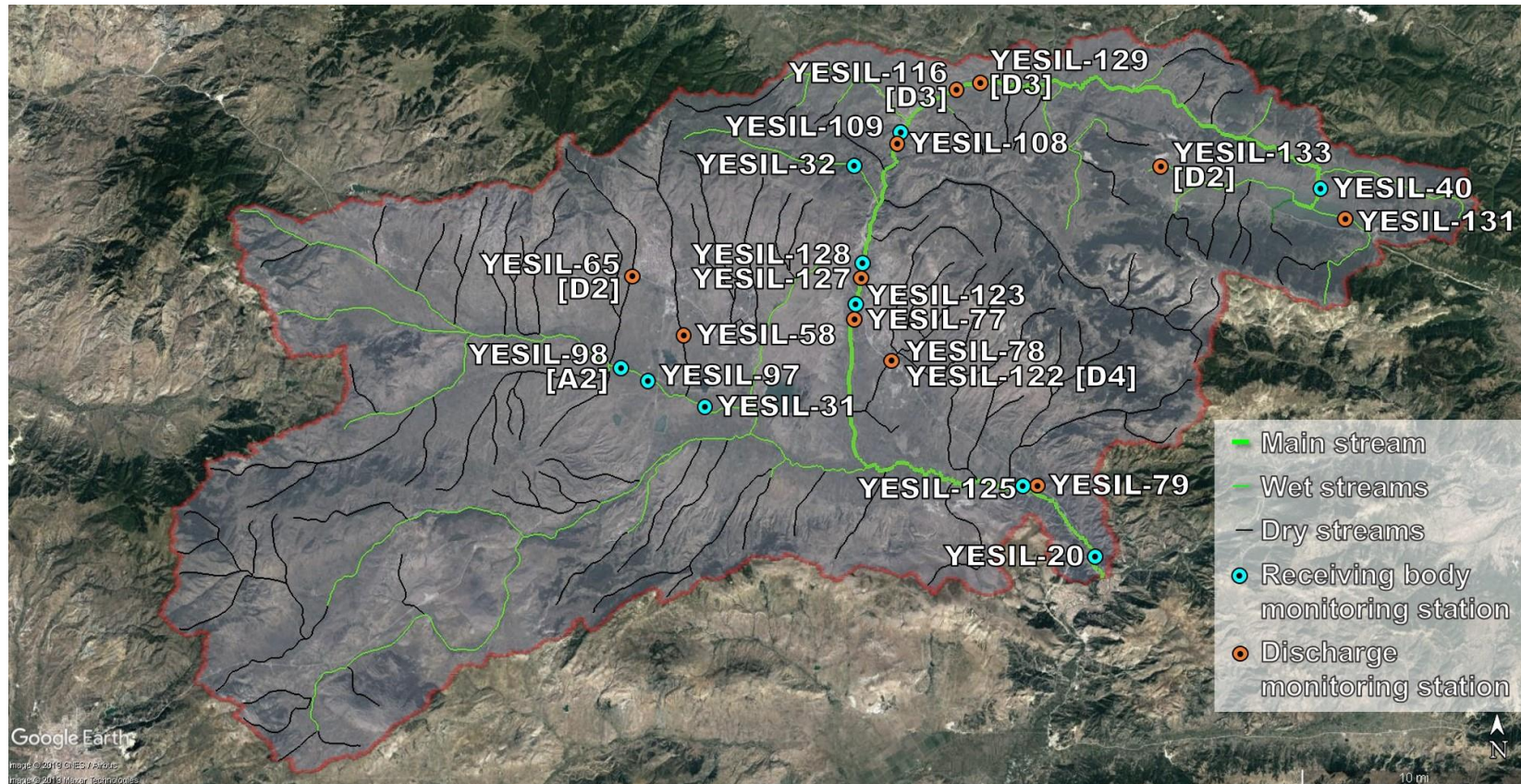


Figure 3.1. A map showing Tersakan sub-basin drainage network and the receiving water body and discharge monitoring stations

D2: receiving water body monitoring station is not available in the upstream of discharge; D3: Effluent discharged to another facility rather than a receiving water body; D4: Planned as a receiving water body monitoring station, however since receiving water body could not be found, the samples were taken from the discharge canal; A2: Only flowrate data is available

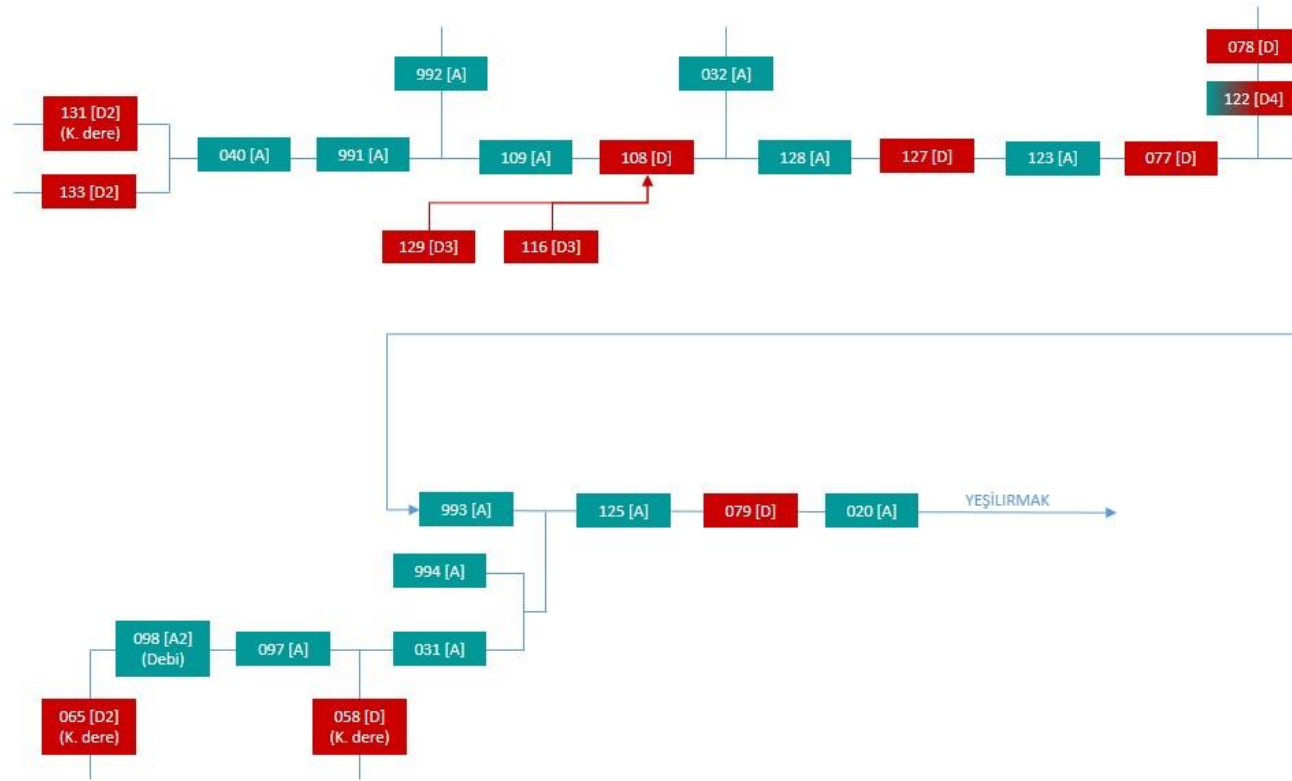


Figure 3.2. All receiving water body and discharge monitoring stations located within Tersakan sub-basin that at least one set of monitoring data have been collected

(D: discharge monitoring station; D2: receiving water body monitoring station is not available in the upstream of discharge; D3: Effluent discharged to another facility rather than a receiving water body; D4: Planned as a receiving water body monitoring station, however since receiving water body could not be found, the samples were taken from the discharge canal, A: receiving water body monitoring station; A2: Only flowrate data is available; K.dere: Dry stream)

Table 3.2. Details about receiving water body (RWB) and discharge monitoring stations (MSs) within Tersakan sub-basin

MS Code	MS Name	Type	Description	MONITORING PERIOD & DATE							
				1 Aug 16	2 Oct 16	3 Feb 17	4 Apr 17	5 Jun 17	6 Aug 17	7 Nov 17	8 Jan 18
YESIL-20	YEOIN015 (Ministry of Forestry and Water Works (MoFWW) Operational Station)	A	RWB MS	+	+	+	+	+	+	+	+
YESIL-31	Merzifon - Old Point (Before Merzifon)	A	RWB MS	+	1	+ ²	1	1	1	1	1
YESIL-32	YEOIN001 (MoFWW Operational Station)	A	RWB MS. Local people informed that sugar factory, slaughterhouse and municipal wastewater are discharged into RWB. Monitoring team observed packing waste on water surface.	+	+	+	+	+	+	+	+
YESIL-40	14-07-00-030 (Ladik Lake Outlet)	A	RWB MS	+	+	+	+	+	+	+	+
YESIL-58	Merzifon/Amasya (Merzifon OIZ)	D	Discharge MS. Upstream of YESIL-31, downstream of Merzifon. Discharged into Gümüşsuyu Brook.			5-10 m ³ /h	? m ³ /h	? m ³ /h	20 m ³ /h	15 m ³ /h	15 m ³ /h
YESIL-65	Meray Oil Industries (Merzifon/Amasya)	D2	Discharge MS. Discharged to dry stream.			5-10 m ³ /h	³	2-3 m ³ /h	³	7.7 m ³ /h	27 m ³ /h
YESIL-77	ET-BİR SULUOVA Slaughterhouse (Suluova-Merkez/Amasya)	D	Discharge MS					2-3 m ³ /h	+ ⁴	+ ⁵	+
								2-3 m ³ /h	2-3 m ³ /h	? m ³ /h	10 m ³ /h

Footnotes are notes taken by the monitoring team during the monitoring seasons. ¹ Since there was no flow, flowrate could not be monitored, sample was taken for the measurement of water quality parameters; ² Pesticide bottle observed in the river. ³ Wastewater is not generated due to facility not being active. ⁴ Sample is taken from a tank where wastewater has probably waited for 3-5 days.

Table 3.2. Details about receiving water body (RWB) and discharge monitoring stations (MSs) within Tersakan sub-basin (cont'd)

MS Code	MS Name	Type	Description	MONITORING PERIOD & DATE							
				1	2	3	4	5	6	7	8
				Aug 16	Oct 16	Feb 17	Apr 17	Jun 17	Aug 17	Nov 17	Jan 18
YESIL-78	Kozlu Food (Suluova-Merkez/Amasya)	D2	Discharge MS. Full performance flowrate of the facility reported as 1.4 m ³ /h.					+	+	+	+
								0.7 m ³ /h	? m ³ /h	0.8-0.9 m ³ /h	2 m ³ /h
YESIL-79	Bakraç Dairy Products (Merkez/Amasya)	D	Discharge station. Only municipal treatment available.					+	+	+	+
								2-3 m ³ /h	8.3 m ³ /h	? m ³ /h	15 m ³ /h
YESIL-97	Upstream of Merzifon OIZ and downstream of Meray Oil Ind.	A	RWB MS						+ ¹	+	+
YESIL-98	Meray Oil Ind. Tributary (Only flowrate)	A2	RWB MS						6	+ ⁷	7
YESIL-108	Havza Municipal WWTP	D	Discharge MS						+ ⁸	+	+ ⁹
									97 m ³ /h	? m ³ /h	? m ³ /h
YESIL-109	Havza Municipal WWTP (From river before the discharge)	A	RWB MS						+	+	+
YESIL-112	Beşgöz Araboğulları Flour Industries	D	Discharge station. Cancelled due to closed facility.								
YESIL-113	Beşgöz Araboğulları Flour Ind. (From river before the discharge)	A	RWB MS. Cancelled due to closed facility.								
YESIL-116	Otat Food Industries	D3	Discharge MS. Discharged to Havza Municipal WWTP.						+	+	+
									70 m ³ /h	? m ³ /h	65 m ³ /h (batch)

Table 3.2. Details about receiving water body (RWB) and discharge monitoring stations (MSs) within Tersakan sub-basin (cont'd)

MS Code	MS Name	Type	Description	MONITORING PERIOD & DATE							
				1	2	3	4	5	6	7	8
				Aug 16	Oct 16	Feb 17	Apr 17	Jun 17	Aug 17	Nov 17	Jan 18
YESIL-117	Otat Food Ind. (From river before the discharge)	A	RWB MS. Cancelled due industrial discharge's transfer to Havza Municipal WWTP.								
YESIL-122	Kozlu Food (From river before the discharge)	D4	Planned as RWB MS, however sample is taken from discharge canal. Since canal's discharge point is unknown, not useful also as a discharge MS.						+	+	+
									1.7 m ³ /h	2 m ³ /h	? m ³ /h
YESIL-123	ET-BİR SULUOVA Slaughterhouse (From river before the discharge)	A	RWB MS						+	+	+
YESIL-125	Bakraç Dairy Products (From river before the discharge)	A	RWB MS							+	+
YESIL-127	Amasya Sugar Factory	D	Discharge MS							+	
										29.2 m ³ /h	
YESIL-128	Amasya Sugar Factory (From river before the discharge)	A	RWB MS							+	
YESIL-129	Aydınoğlu Flour and Food Industries	D3	Discharge MS. Discharged to Havza Municipal WWTP.							+	+
										1 m ³ /h	10 m ³ /h
YESIL-130	Aydınoğlu Flour and Food Ind. (From river before the discharge)	A	RWB MS. Cancelled due industrial discharge's transfer to Havza Municipal WWTP.								

Table 3.2. Details about receiving water body (RWB) and discharge monitoring stations (MSs) within Tersakan sub-basin (cont'd)

MS Code	MS Name	Type	Description	MONITORING PERIOD & DATE							
				1	2	3	4	5	6	7	8
				Aug 16	Oct 16	Feb 17	Apr 17	Jun 17	Aug 17	Nov 17	Jan 18
YESIL-117	Otat Food Ind. (From river before the discharge)	A	RWB MS. Cancelled due industrial discharge's transfer to Havza Municipal WWTP.								
YESIL-122	Kozlu Food (From river before the discharge)	D4	Planned as RWB MS, however sample is taken from discharge canal. Since canal's discharge point is unknown, not useful also as a discharge MS.						+	+	+
									1.7 m ³ /h	2 m ³ /h	? m ³ /h
YESIL-123	ET-BİR SULUOVA Slaughterhouse (From river before the discharge)	A	RWB MS						+	+	+
YESIL-125	Bakraç Dairy Products (From river before the discharge)	A	RWB MS							+	+
YESIL-127	Amasya Sugar Factory	D	Discharge MS							+	
										29.2 m ³ /h	
YESIL-128	Amasya Sugar Factory (From river before the discharge)	A	RWB MS							+	
YESIL-129	Aydınoglu Flour and Food Industries	D3	Discharge MS. Discharged to Havza Municipal WWTP.							+	+
										1 m ³ /h	10 m ³ /h
YESIL-130	Aydınoglu Flour and Food Ind. (From river before the discharge)	A	RWB MS. Cancelled due industrial discharge's transfer to Havza Municipal WWTP.								

Table 3.2. Details about receiving water body (RWB) and discharge monitoring stations (MSs) within Tersakan sub-basin (cont'd)

MS Code	MS Name	Type	Description	MONITORING PERIOD & DATE							
				1	2	3	4	5	6	7	8
				Aug 16	Oct 16	Feb 17	Apr 17	Jun 17	Aug 17	Nov 17	Jan 18
YESIL-131	Doğa Su Food Industries	D2	Discharge MS							+	+
										0.8 m ³ /h	2 m ³ /h
YESIL-132	Doğa Su Food Ind. (From river before the discharge)	A	RWB MS							10	11
YESIL-133	Akçansa Cement Industries - Ladik Branch	D2	Discharge MS. Cancelled after one monitoring period due to generating only municipal wastewater.							+	
										45 m ³ /h	
YESIL-134	Akçansa Cement Ind. (From river before the discharge)	A	RWB MS. Cancelled due to generating only municipal wastewater.								
YESIL-136	Amasya Sanitary Landfill	D	Discharge MS. Removed from Tersakan sub-basin list due to leachate being transferred to Amasya WWTP which is out of bounds.								
A-01	Tersakan New RWB MS 1	A	RWB MS								+
A-02	Tersakan New RWB MS 2	A	RWB MS								+
A-03	Tersakan New RWB MS 3	A	RWB MS								+
A-04	Tersakan New RWB MS 4	A	RWB MS								+

Footnotes are notes taken by the monitoring team during the monitoring seasons. ⁵ Sample is taken from a tank where wastewater has waited 1 day. ⁶ Meray Oil Ind. was not visited on the 6th tour due to not being active. ⁷ Cancellation of the MS was demanded since width of the river was 1 m and there was no flow. ⁸ Sample is taken from sedimentation tank weir due to maintenance. ⁹ Wastewater that had waited a while was taken as sample due to facility not being active for the past 7 days. ¹⁰ River was dry during this period of monitoring, flow is only seen in the case of rainfall. ¹¹ River was dry during monitoring period. Weather conditions indicate possible freezing. D: discharge MS; D2: RWB MS is not available in the upstream of discharge; D3: Effluent discharged to another facility rather than a RWB; D4: Planned as a RWB MS. however since RWB could not be found. the samples were taken from the discharge canal. A: RWB MS; A2: Only flowrate data is available

Figure 3.2 shows that only 5 couples of receiving water body-discharge monitoring stations are suitable for the discharge limit establishment study. Information regarding these couples are provided in Table 3.3.

Table 3.3. *Monitoring station couples within Tersakan sub-basin that are suitable for discharge limit estimation studies*

Couple No.	Discharge MS Code	Discharge MS Name	Periods Monitored (TNPM ¹)	RWB MS Code	RWB MS Name	Periods Monitored (TNPM ¹)
1	YESIL-58	Merzifon/Amasya (Merzifon OIZ)	3-4-5-6-7-8 (6)	YESIL-97	Upstream of Merzifon OIZ and downstream of Meray Oil Ind.	7-8 (2)
2	YESIL-77	ET-BİR SULUOVA Slaughterhouse (Suluova-Merkez/Amasya)	5-6-7-8 (4)	YESIL-123	ET-BİR SULUOVA Slaughterhouse (From river before the discharge)	6-7-8 (3)
3	YESIL-79	Bakraç Dairy Products (Merkez/Amasya)	7-8 (2)	YESIL-125	Bakraç Dairy Products (From river before the discharge)	7-8 (2)
4	YESIL-108	Havza Municipal WWTP	6-7-8 (3)	YESIL-109	Havza Municipal WWTP (From river before the discharge)	6-7-8 (3)
5	YESIL-127	Amasya Sugar Factory	7 (1)	YESIL-128	Amasya Sugar Factory (From river before the discharge)	7 (1)

¹ TNPM: Total number of periods monitored; RWB: receiving water body; MS: monitoring station

The first couple which are YESIL-58 and YESIL-97, are not an ideal couple for the study since the effluent of Merzifon OIZ WWTP is actually discharge into a dry stream. However, owing to the constraint of useful data, this couple is not excluded.

3.2. Data Collection and Preparation

Field monitoring studies have been conducted for the collection of hydro-geometric and river water quality data as well as wastewater discharge characterization in the Tersakan sub-basin for 8 seasons (Aug-2016, Oct-2016, Feb-2017, Apr-2017, Jun-2017, Aug-2017, Nov-2017, Jan-2018). The collected raw data have been subjected to a preliminary analysis to make the data suitable for using in the application of the newly developed tool for EQS-based discharge limit establishment (see Chapter 4).

This work includes the estimation of the following for each monitoring station and season:

- Hydro-geometric parameters such as river depth (d , equation 11), width (w , equation 12), cross-sectional area (A , equation 9), and channel slope (S)
- Hydrodynamic parameters such as flowrate (Q) and mean velocity (v , equation 10) for each receiving water body monitoring station and season
- River mixing parameters such as shear velocity (u^* , equation 17), longitudinal dispersion coefficient (D_x , equation 32), transverse dispersion coefficient (D_y , 26), vertical shear dispersion coefficient (K_z , equation 18), vertical characteristic mixing distance (L_z , equation 34), transverse characteristic mixing distance (L_y , equation 35), Peclet number (Pe , equation 37), Damkohler numbers (Da^I , Da^{II} , equations 38 and 39 respectively)

The methodology followed for the calculation of cross-sectional area, flowrate, mean velocity, mean depth and the estimation of channel slope is explained below.

For each monitoring station, the river is divided into approximately equally spaced transverse sections. Data is collected as transverse distance from one bank of the river, total depth corresponding to that specific transverse location and velocity values at different vertical locations at that specific transverse location.

Local velocity values are first multiplied with the corresponding vertical intervals to obtain the areas of lower trapezoids or triangles (equation 6). The sum of these values for each transverse interval are represented as the upper vertical green lines in Figure 3.3 (q values, equation 7). Then these summed values are multiplied with the transverse intervals in order to obtain the areas of the upper trapezoids or triangles. Lastly all the upper areas are summed up to obtain the flowrate, Q (equation 8).

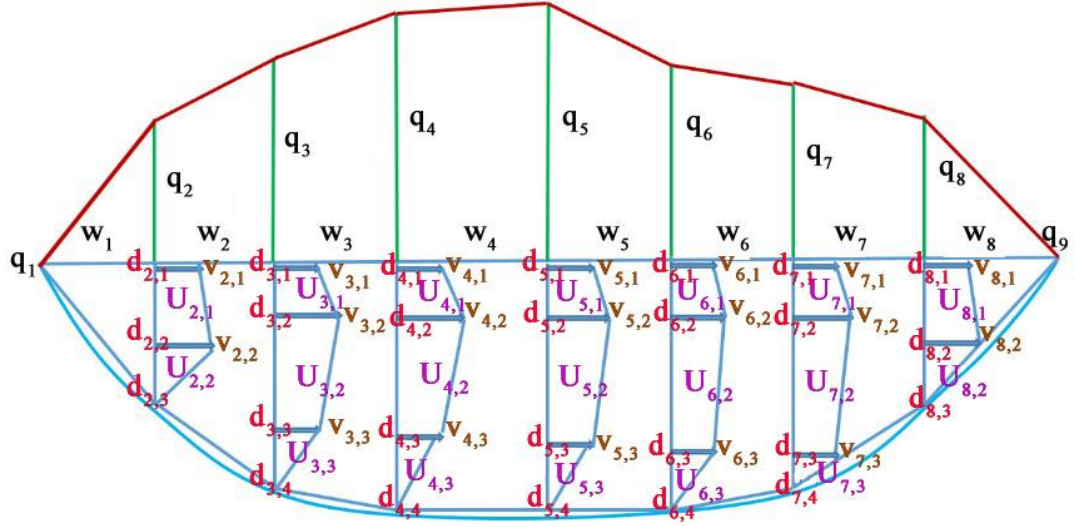


Figure 3.3. Flowrate approximation

$$U_{i,j-1} = \frac{(d_{i,j} - d_{i,j-1})(v_{j-1} + v_j)}{2} \text{ for } 2 \leq j \leq j_{\text{final}} \text{ and } 1 \leq i \leq i_{\text{final}} \quad (6)$$

$$q_i = \left(\sum_{j=1}^{j_{\text{final}}-1} U_{i,j} \right) \text{ for } 1 \leq i \leq i_{\text{final}} \quad (7)$$

$$Q = \sum_{i=1}^{i_{\text{final}}-1} \frac{(q_i + q_{i+1})w_i}{2} \quad (8)$$

$U_{i,j}$ is the first local factor for flowrate estimation [L^2/T], $d_{i,j}$ is the local depth [L], v_j is the local velocity [L/T], q_i is the second local factor for flowrate estimation [L^2/T], w_i is the local width [L] and Q is the flowrate [L^3/T].

Data collected for flowrate approximation is used also to approximate the cross-sectional areas, A . The cross-section is divided into right triangles and trapezoids, the areas of these are summed (see Figure 3.4).

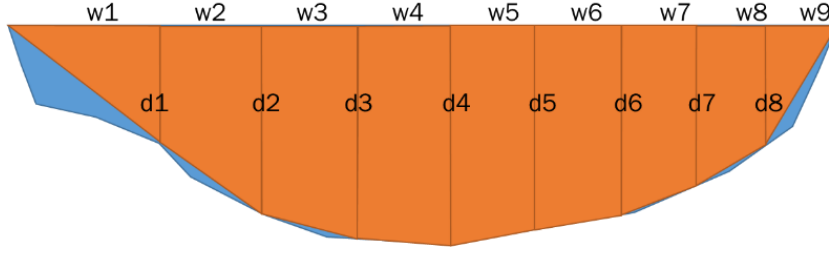


Figure 3.4. Cross-sectional area approximation

$$A = \sum_{i=1}^n \frac{d_1 w_1 + (d_{i-1} + d_i) w_i + d_n w_{n+1}}{2} \quad (9)$$

where d_i is local depth [L].

Mean velocity, v , is approximated as a weighted-average which favors larger, near surface values of velocity, since it is assumed that these values represent the advective transport process better (see also Figure 3.3).

$$v = \frac{\sum_i \sum_j U_{i,j} v_{i,j}}{\sum_i \sum_j U_{i,j}} \quad (10)$$

Mean depth, d , is approximated as arithmetic-average of non-zero local depth values along the width of the river (see also Figure 3.4).

$$d = \frac{\sum_{i=1}^m d_i}{m} \quad (11)$$

Width, w , values are the measured transverse distance from one bank of the river to the other (see Figure 3.4).

$$w = \sum_{i=1}^n w_i \quad (12)$$

For the estimation of these parameters from raw receiving water body monitoring data, MATLAB codes are developed and implemented (see Appendix B for the details).

River hydro-geometric and hydrodynamic parameters estimated for all receiving water body monitoring stations per each season and averaged values for each station are given in Table 3.4 and Table 3.5, respectively.

Table 3.4. Values of measured width (w) and calculated mean velocity (v), depth (d), width/depth ratio (w/d), cross-sectional area (A) and flowrate (Q) for receiving water body monitoring stations within Tersakan sub-basin (season-wise)

Station ID	Season	w (m)	v (m/s)	d (m)	w/d	A (m ²)	Q (m ³ /s)
20	2016-08	1.61E+01	7.51E-01	4.04E-01	40	5.59E+00	3.10E+00
31	2016-08	2.61E+00	1.18E-01	5.68E-01	5	1.29E+00	1.17E-01
32	2016-08	1.80E+01	7.39E-01	1.51E-01	119	2.42E+00	1.07E+00
40	2016-08	1.32E+01	9.94E-01	7.65E-01	17	8.92E+00	6.26E+00
20	2016-10	1.40E+01	7.20E-01	2.44E-01	57	2.99E+00	1.45E+00
32	2016-10	7.40E+00	5.45E-01	2.53E-01	29	1.45E+00	5.28E-01
40	2016-10	1.10E+01	2.25E-01	2.20E-01	50	1.87E+00	1.82E-01
20	2017-02	1.40E+01	4.69E-01	3.10E-01	45	3.40E+00	1.00E+00
31	2017-02	1.85E+00	1.62E-01	4.57E-01	4	6.50E-01	4.47E-02
32	2017-02	1.00E+01	4.69E-01	1.30E-01	77	1.04E+00	3.14E-01
40	2017-02	1.03E+01	1.21E-01	2.80E-01	37	2.34E+00	1.77E-01
20	2017-04	1.52E+01	8.50E-01	4.67E-01	33	5.41E+00	2.85E+00
32	2017-04	6.70E+00	4.01E-01	2.80E-01	24	1.54E+00	3.33E-01
40	2017-04	1.03E+01	1.26E-01	1.22E-01	84	1.15E+00	7.91E-02
20	2017-06	1.43E+01	6.92E-01	3.17E-01	45	3.49E+00	1.72E+00
32	2017-06	1.11E+01	6.63E-01	1.60E-01	69	1.58E+00	4.85E-01
40	2017-06	1.10E+01	3.90E-01	3.10E-01	35	2.64E+00	6.92E-01
20	2017-08	1.40E+01	9.61E-01	3.95E-01	35	3.76E+00	2.57E+00
32	2017-08	1.25E+01	8.53E-01	1.67E-01	75	1.91E+00	8.59E-01
40	2017-08	1.14E+01	3.33E-01	2.73E-01	42	2.38E+00	4.54E-01
109	2017-08	1.08E+01	6.13E-01	3.40E-01	32	2.80E+00	1.14E+00
123	2017-08	1.20E+01	1.16E-01	5.05E-01	24	4.15E+00	9.09E-02
20	2017-12	1.04E+01	6.56E-01	3.50E-01	30	2.88E+00	1.29E+00
32	2017-12	6.00E+00	7.65E-01	1.65E-01	36	4.95E-01	2.63E-01
40	2017-12	9.40E+00	6.91E-01	1.53E-01	61	1.33E+00	1.71E-01
97	2017-12	2.70E+00	9.76E-02	1.85E-01	15	3.37E-01	1.40E-02

Table 3.4. Values of measured width (w) and calculated mean velocity (v), depth (d), width/depth ratio (w/d), cross-sectional area (A) and flowrate (Q) for receiving water body monitoring stations within Tersakan sub-basin (season-wise) (cont'd)

Station ID	Season	w (m)	v (m/s)	d (m)	w/d	A (m ²)	Q (m ³ /s)
98	2017-12	1.20E+00	3.68E-01	1.30E-01	9	1.17E-01	2.04E-02
109	2017-12	1.20E+01	8.89E-01	1.67E-01	72	1.50E+00	9.82E-01
123	2017-12	7.50E+00	3.78E-01	2.25E-01	33	1.16E+00	2.65E-01
125	2017-12	1.05E+01	5.47E-01	3.07E-01	34	2.55E+00	9.44E-01
128	2017-12	5.00E+00	3.01E-01	1.05E-01	48	3.75E-01	6.91E-02
20	2018-01	1.10E+01	6.26E-01	1.97E-01	56	1.65E+00	7.12E-01
32	2018-01	7.00E+00	6.95E-01	1.03E-01	68	6.00E-01	2.71E-01
40	2018-01	1.00E+01	9.48E-02	1.63E-01	61	1.37E+00	8.00E-02
97	2018-01	5.00E+00	3.72E-01	1.85E-01	27	5.40E-01	1.05E-01
109	2018-01	1.05E+01	9.69E-01	2.87E-01	37	2.36E+00	1.71E+00
123	2018-01	7.00E+00	4.34E-01	2.85E-01	25	1.39E+00	4.25E-01
125	2018-01	9.50E+00	2.74E-01	2.30E-01	41	1.68E+00	2.72E-01
991	2018-01	1.08E+01	4.95E-01	4.17E-01	26	3.42E+00	1.31E+00
992	2018-01	6.80E+00	1.01E+00	2.27E-01	30	1.23E+00	8.23E-01
993	2018-01	2.15E+01	6.08E-01	1.23E-01	176	2.07E+00	6.77E-01
994	2018-01	2.50E+00	4.98E-01	8.00E-02	31	1.38E-01	3.54E-02

Table 3.5. Values of measured width (w) and calculated mean velocity (v), depth (d), width/depth ratio (w/d), cross-sectional area (A) and flowrate (Q) for receiving water body monitoring stations within Tersakan sub-basin (average)

Station ID	w (m)	v (m/s)	d (m)	w/d	A (m ²)	Q (m ³ /s)
20	1.36E+01	7.15E-01	3.35E-01	41	3.64E+00	1.84E+00
31	2.23E+00	1.40E-01	5.12E-01	4	9.72E-01	8.06E-02
32	9.83E+00	6.41E-01	1.76E-01	56	1.38E+00	5.16E-01
40	1.08E+01	3.72E-01	2.86E-01	38	2.75E+00	1.01E+00
97	3.85E+00	2.35E-01	1.85E-01	21	4.39E-01	5.96E-02
98	1.20E+00	3.68E-01	1.30E-01	9	1.17E-01	2.04E-02
109	1.11E+01	8.24E-01	2.64E-01	42	2.22E+00	1.28E+00
123	8.83E+00	3.09E-01	3.38E-01	26	2.23E+00	2.60E-01
125	1.00E+01	4.10E-01	2.68E-01	37	2.12E+00	6.08E-01
128	5.00E+00	3.01E-01	1.05E-01	48	3.75E-01	6.91E-02
991	1.08E+01	4.95E-01	4.17E-01	26	3.42E+00	1.31E+00
992	6.80E+00	1.01E+00	2.27E-01	30	1.23E+00	8.23E-01
993	2.15E+01	6.08E-01	1.23E-01	176	2.07E+00	6.77E-01
994	2.50E+00	4.98E-01	8.00E-02	31	1.38E-01	3.54E-02

Channel slope is also an important receiving water body parameter for discharge limit and mixing zone estimation because it is used to approximate shear velocity which is essential for the estimation of many other river mixing parameters (see Chapter 4 for the details). Channel slope around each receiving body monitoring station was estimated using ArcMap software. 30 m digital-elevation-model (DEM) obtained from the Turkish Ministry of Defense's General Command of Mapping, the coordinates of the stations and aerial photos taken from Google Earth are input to the software. 1 km upstream and downstream of each station is divided into equally spaced intervals of 100-m and slope is estimated from the variations of elevation between each of these 100-m intervals read from the DEM. Arithmetic-average of all non-zero slope values obtained for each station are taken as the channel slope [33]. Approximated channel slope values for the receiving water body monitoring stations within Tersakan can be found in Table 3.6.

Table 3.6. *Channel slope values for each receiving body monitoring station within Tersakan sub-basin*

Station ID	20	31	32	40	97	98	109
Slope	0.005	0.0075	0.0195	0.0045	0.005	0.0125	0.003
Station ID	123	125	128	991	992	993	994
Slope	0.006	0.004	0.007	0.0055	0.0085	0.003	0.01

The methods of approximation for parameters related to river mixing are explained in detail on Chapter 4, however to keep data related to the study site together, values estimated for shear velocity (u^*), longitudinal dispersion coefficient (D_x), transverse dispersion coefficient (D_y), vertical shear dispersion coefficient (K_z), vertical characteristic mixing distance (L_z), transverse characteristic vertical mixing distance (L_y) and Peclet number (Pe) are presented in Table 3.7 (season-wise) and Table 3.8 (average).

Table 3.7. Estimations obtained for shear velocity (u^*), longitudinal dispersion coefficient (D_x), transverse dispersion coefficient (D_y), vertical shear dispersion coefficient (K_z), vertical characteristic mixing distance (L_z), transverse characteristic mixing distance (L_y) and Pe for receiving water body monitoring stations along Tersakan Creek (season-wise)

Station ID	Season	u^* (m/s)	D_x (m ² /s)	D_y (m ² /s)	K_z (m ² /s)	L_z (m)	L_y (m)	Pe
20	2016-08	1.41E-01	3.62E+01	2.22E-02	3.80E-03	4.85E+00	7.02E+02	15
31	2016-08	2.04E-01	6.34E-02	1.70E-02	7.80E-03	6.81E+00	3.80E+00	7
32	2016-08	1.70E-01	2.50E+01	2.69E-02	1.70E-03	1.82E+00	7.10E+02	21
40	2016-08	1.84E-01	3.98E+01	3.14E-02	9.40E-03	9.18E+00	4.42E+02	11
20	2016-10	1.10E-01	2.87E+01	1.72E-02	1.80E-03	2.93E+00	6.56E+02	16
32	2016-10	2.20E-01	8.10E+00	1.22E-02	3.70E-03	3.04E+00	1.95E+02	13
40	2016-10	9.85E-02	4.99E+00	6.30E-03	1.50E-03	2.64E+00	3.48E+02	16
20	2017-02	1.23E-01	1.68E+01	1.35E-02	2.60E-03	3.72E+00	5.45E+02	15
31	2017-02	1.83E-01	8.62E-02	1.23E-02	5.60E-03	5.48E+00	3.61E+00	7
32	2017-02	1.58E-01	9.79E+00	9.90E-03	1.40E-03	1.56E+00	3.79E+02	18
40	2017-02	1.11E-01	1.49E+00	5.90E-03	2.10E-03	3.36E+00	1.74E+02	14
20	2017-04	1.51E-01	4.08E+01	2.40E-02	4.70E-03	5.60E+00	6.54E+02	14
32	2017-04	2.31E-01	3.93E+00	1.19E-02	4.30E-03	3.36E+00	1.21E+02	12
40	2017-04	7.34E-02	2.19E+00	3.30E-03	6.00E-04	1.46E+00	3.25E+02	19
20	2017-06	1.25E-01	2.91E+01	1.77E-02	2.60E-03	3.80E+00	6.40E+02	15
32	2017-06	1.75E-01	1.70E+01	1.45E-02	1.90E-03	1.92E+00	4.48E+02	18
40	2017-06	1.17E-01	1.05E+01	1.00E-02	2.40E-03	3.72E+00	3.78E+02	14
20	2017-08	1.39E-01	4.53E+01	2.28E-02	3.70E-03	4.74E+00	6.61E+02	14
32	2017-08	1.79E-01	2.54E+01	1.99E-02	2.00E-03	2.00E+00	5.35E+02	18
40	2017-08	1.10E-01	8.85E+00	8.80E-03	2.00E-03	3.28E+00	3.93E+02	15
109	2017-08	1.00E-01	2.18E+01	1.19E-02	2.30E-03	4.08E+00	4.79E+02	14
123	2017-08	1.72E-01	9.10E-01	1.39E-02	5.80E-03	6.06E+00	9.60E+01	12
20	2017-12	1.31E-01	2.06E+01	1.37E-02	3.10E-03	4.20E+00	4.15E+02	13
32	2017-12	1.78E-01	1.27E+01	9.40E-03	2.00E-03	1.98E+00	2.35E+02	14
40	2017-12	8.23E-02	1.88E+01	1.06E-02	8.00E-04	1.84E+00	4.59E+02	17
97	2017-12	9.53E-02	1.93E-01	2.80E-03	1.20E-03	2.22E+00	2.06E+01	10
98	2017-12	1.26E-01	6.52E-01	2.70E-03	1.10E-03	1.56E+00	1.59E+01	9
109	2017-12	7.00E-02	3.00E+01	1.71E-02	8.00E-04	2.00E+00	5.99E+02	18
123	2017-12	1.15E-01	6.87E+00	6.80E-03	1.70E-03	2.70E+00	2.50E+02	14
125	2017-12	1.10E-01	1.71E+01	1.11E-02	2.30E-03	3.68E+00	4.34E+02	14
128	2017-12	8.49E-02	3.72E+00	3.10E-03	6.00E-04	1.26E+00	1.91E+02	15
20	2018-01	9.82E-02	1.97E+01	1.18E-02	1.30E-03	2.36E+00	5.12E+02	16
32	2018-01	1.41E-01	1.21E+01	9.00E-03	1.00E-03	1.24E+00	3.04E+02	17

Table 3.7. Estimations obtained for shear velocity (u^*), longitudinal dispersion coefficient (D_x), transverse dispersion coefficient (D_y), vertical shear dispersion coefficient (K_z), vertical characteristic mixing distance (L_z), transverse characteristic mixing distance (L_y) and Pe for receiving water body monitoring stations along Tersakan Creek (season-wise) (cont'd)

Station ID	Season	u^* (m/s)	D_x (m ² /s)	D_y (m ² /s)	K_z (m ² /s)	L_z (m)	L_y (m)	Pe
40	2018-01	8.49E-02	1.30E+00	3.30E-03	9.00E-04	1.96E+00	2.30E+02	17
97	2018-01	9.53E-02	4.90E+00	4.40E-03	1.20E-03	2.22E+00	1.69E+02	13
109	2018-01	9.19E-02	3.85E+01	1.52E-02	1.80E-03	3.44E+00	5.63E+02	14
123	2018-01	1.30E-01	7.20E+00	8.30E-03	2.50E-03	3.42E+00	2.06E+02	12
125	2018-01	9.50E-02	5.92E+00	6.20E-03	1.50E-03	2.76E+00	3.19E+02	15
991	2018-01	1.50E-01	1.27E+01	1.43E-02	4.20E-03	5.00E+00	3.23E+02	13
992	2018-01	1.38E-01	2.46E+01	1.17E-02	2.10E-03	2.72E+00	3.22E+02	13
993	2018-01	6.00E-02	2.08E+01	2.75E-02	5.00E-04	1.47E+00	8.17E+02	24
994	2018-01	8.86E-02	3.95E+00	2.30E-03	5.00E-04	9.60E-01	1.07E+02	13

Table 3.8. Estimations obtained for shear velocity (u^*), longitudinal dispersion coefficient (D_x), transverse dispersion coefficient (D_y), vertical shear dispersion coefficient (K_z), vertical characteristic mixing distance (L_z), transverse characteristic mixing distance (L_y) and Pe for receiving water body monitoring stations along Tersakan Creek (average)

Station ID	u^* (m/s)	D_x (m ² /s)	D_y (m ² /s)	K_z (m ² /s)	L_z (m)	L_y (m)	Pe
20	1.28E-01	2.95E+01	1.76E-02	2.88E-03	2.23E+00	6.05E+02	15
31	1.94E-01	7.71E-02	1.46E-02	6.66E-03	4.42E-01	3.83E+00	7
32	1.84E-01	1.51E+01	1.29E-02	2.17E-03	7.35E-01	3.83E+02	16
40	1.12E-01	9.83E+00	9.21E-03	2.15E-03	1.13E+00	3.79E+02	14
97	9.53E-02	2.55E+00	3.60E-03	1.20E-03	5.44E-01	9.47E+01	12
98	1.26E-01	6.52E-01	2.67E-03	1.10E-03	4.52E-01	1.59E+01	9
109	8.82E-02	3.01E+01	1.47E-02	1.63E-03	2.88E+00	5.47E+02	15
123	1.41E-01	4.91E+00	9.60E-03	3.20E-03	8.85E-01	2.01E+02	13
125	1.03E-01	1.15E+01	8.65E-03	1.90E-03	1.31E+00	3.76E+02	14
128	8.49E-02	3.72E+00	3.10E-03	6.00E-04	4.44E-01	1.91E+02	15
991	1.50E-01	1.27E+01	1.43E-02	4.19E-03	1.64E+00	3.23E+02	13
992	1.37E-01	2.46E+01	1.17E-02	2.09E-03	2.00E+00	3.22E+02	13
993	6.00E-02	2.08E+01	2.75E-02	4.93E-04	1.48E+00	8.17E+02	24
994	8.86E-02	3.95E+00	2.34E-03	4.75E-04	5.37E-01	1.07E+02	13

The concept of an EQS-based discharge limit (maximum discharge concentration of a CoC that would ensure a receiving water body concentration less than the EQS value of that CoC at the end of the mixing zone, see Chapter 4 for details) is only valid under the condition where the concentration of a CoC is greater than its EQS value at the discharge monitoring station and less than its EQS value at the relevant receiving water body monitoring station. All water quality parameters that have EQS values set on the Turkish Surface Water Quality Regulation including 16 conventional parameters, 45 priority substances and 250 specific pollutants were monitored for all receiving water bodies and discharge MSs as part of the monitoring program. 99 out of 311 of these parameters have been observed at least once at any one monitoring station among the five MS couples within Tersakan sub-basin that are selected for the application of the discharge limit estimated approach (see Table 3.3), 58 of the 99 observed parameters never exceed their relevant EQS values. 10 out of the 41 rest have EQS values less than the limit of detection (LOD) of the relevant method of measurement, therefore they have concentration values greater than the EQS value in all stations. 9 out of the 31 remaining have observed concentration values greater than the EQS values in all stations. Also 3 of these monitored parameters do not have EQS values specified. Consequently only 19 out of the 311 monitored parameters are valid at any receiving water body-discharge MS couple selected for the application of the approach. Suitability status of these 19 CoCs for each one of the previously selected 5 monitoring station couples are given in Figure 3.5.

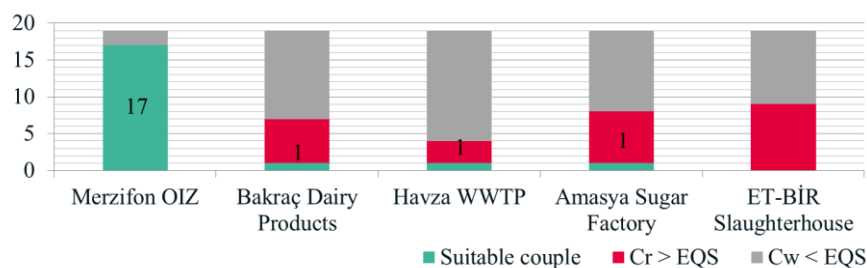


Figure 3.5. A chart showing the suitability of the concentrations of the 19 CoCs in the receiving water body and the discharge the five receiving water body-discharge monitoring station couples previously selected

Eventually, 20 distinct cases of discharges of particular CoCs at the previously selected couples of discharge-receiving water body monitoring stations are found to be suitable for the utilization of the discharge limit establishment approach. Details about these cases are given in Table 3.9.

Table 3.9. Details about the 20 particular discharges that are suitable for discharge limit estimation studies within the Tersakan sub-basin (average)

No	Station Name	RWB-Dis. MS Numbers	Contaminant Name	EQS	C _w	Q _w (m ³ /s)	C _r	Q _r (m ³ /s)
1	Merzifon OIZ	97 - 58	Nonylphenol (µg/L)	3.00E-01	7.61E-01	3.99E-03	5.00E-04	5.96E-02
2	Merzifon OIZ	97 - 58	Tridecane (µg/L)	5.00E-02	1.48E+00	3.99E-03	1.00E-02	5.96E-02
3	Merzifon OIZ	97 - 58	TP (mg/L)	1.60E-01	1.94E+00	3.99E-03	1.28E-01	5.96E-02
4	Merzifon OIZ	97 - 58	TOC (mg/L)	8.00E+00	2.35E+01	3.99E-03	2.09E+00	5.96E-02
5	Merzifon OIZ	97 - 58	Ni (µg/L)	4.00E+00	9.94E+01	3.99E-03	1.47E+00	5.96E-02
6	Merzifon OIZ	97 - 58	COD (mg/L)	5.00E+01	1.14E+02	3.99E-03	1.05E+01	5.96E-02
7	Merzifon OIZ	97 - 58	NH ₄ -N (mg/L)	1.00E+00	2.19E+01	3.99E-03	1.03E-01	5.96E-02
8	Merzifon OIZ	97 - 58	Cd (µg/L)	8.00E-02	1.71E-01	3.99E-03	2.95E-02	5.96E-02
9	Merzifon OIZ	97 - 58	Free CN (µg/L)	1.20E+00	9.54E+00	3.99E-03	5.00E-01	5.96E-02
10	Merzifon OIZ	97 - 58	Ti (µg/L)	2.60E+01	3.73E+01	3.99E-03	3.84E+00	5.96E-02
11	Merzifon OIZ	97 - 58	Petroleum hydrocarbons	9.60E+01	3.02E+02	3.99E-03	8.40E+01	5.96E-02
12	Merzifon OIZ	97 - 58	B (µg/L)	7.07E+02	1.28E+03	3.99E-03	2.91E+02	5.96E-02
13	Merzifon OIZ	97 - 58	Benzo(a)pyrene (µg/L)	1.70E-04	2.00E-04	3.99E-03	1.00E-04	5.96E-02
14	Merzifon OIZ	97 - 58	4-Chloroaniline (µg/L)	5.00E-03	6.30E-03	3.99E-03	2.50E-03	5.96E-02
15	Merzifon OIZ	97 - 58	Diphenyl ether; diphenyl oxide (µg/L)	6.00E+00	7.84E+00	3.99E-03	5.00E-04	5.96E-02
16	Merzifon OIZ	97 - 58	Ethylfluralin (µg/L)	3.00E-01	1.09E+00	3.99E-03	2.50E-03	5.96E-02
17	Merzifon OIZ	97 - 58	Fenpropimorph (µg/L)	1.00E-01	1.45E-01	3.99E-03	5.00E-02	5.96E-02
18	Havza Municipal WWTP	109 - 108	TOC (mg/L)	8.00E+00	9.83E+00	2.69E-02	4.89E+00	1.28E+00
19	Bakrac Dairy Products	125 - 79	TDS (mg/L)	1.50E+03	2.78E+03	8.87E-03	1.36E+03	6.08E-01
20	Amasya Sugar Factory	128 - 127	Bis(2-ethylhexyl) terephthalate (µg/L)	1.00E-01	1.15E+00	8.11E-03	5.00E-04	6.91E-02

RWB: Receiving water body; MS: Monitoring station; EQS: Environmental quality standard; C_w: Discharge concentration of the CoC; Q_w: Discharge flowrate; C_r: Receiving water body concentration of the CoC; Q_r: Receiving water body flowrate

For the estimation of discharge limits, the potentials of biodegradation for the CoCs given in Table 3.9 are also required to be known. Thus, biodegradation half-lives for the 19 parameters observed within Tersakan sub-basin are examined from the literature. Assuming first-order kinetics, the biodegradation constants are also calculated from the half-lives according to the below relationship, using the maximum values from the ranges given for half-lives to reach the most conservative approach [34] (see Table 3.10 for relevant information):

$$k = \frac{0.693}{t_{1/2}} \quad (13)$$

where k is the first-order biodegradation constant [$1/T$], and $t_{1/2}$ is the half-life [T].

Table 3.10. *Half-lives and first-order biodegradation constants for the CoCs observed within Tersakan sub-basin that can be found in the literature*

Contaminant Name	Range of half-lives	Calculated constant k (s^{-1})	Reference
Nonylphenol	2.5 - 56 d	1.43E-07	[35]
4-Chloroaniline	0.3 - 347 d	2.31E-08	[35]
Diphenyl ether	4 h	4.81E-05	[35]
Fenpropimorph	13 d	6.17E-07	[36]
Ethalfuralin	0.1 - 2 d (pond)	4.01E-06	[37]

All biodegradation information given in Table 3.10, are related to Merzifon OIZ discharge. Both advective and dispersive Damkohler numbers (estimated via equations 38 and 39 respectively) related to the discharge then, is given in Table 3.11.

Table 3.11. *Advective and dispersive Damkohler numbers (Da^I and Da^{II} , respectively) related to selected CoCs found to be suitable for discharge limit establishment in Merzifon OIZ discharge*

Contaminant Name	Da^I (adv)	Da^{II} (disp)
Nonylphenol	5.77E-05	5.04E-04
4-Chloroaniline	9.32E-06	8.14E-05
Diphenyl ether	1.94E-02	1.69E-01
Fenpropimorph	2.49E-04	2.17E-03
Ethalfuralin	1.62E-03	1.41E-02

With these last two chapters, the motivation behind the EQS-based discharge limit estimation approach that is developed as part of this study has been expressed and the fundamental requirements of it have been clearly identified and also met by the preparation of the monitoring data in this chapter.

CHAPTER 4

A NOVEL APPROACH TO DISCHARGE LIMIT ESTIMATION

An effluent discharged to a natural stream undergoes mixing along the depth of the river in the vertical -direction, along the width in the transverse direction and along the length in the longitudinal direction. Furthermore, organic pollutants in the effluent will also be subjected to various degradation processes (biological, chemical etc.). After the discharge, due to the effects of vertical dispersion and the fact that the depth is the smallest dimension of rivers, contaminants complete their mixing along the depth in a short while. The distance that needs to be travelled by the contaminants along the flow direction to achieve complete mixing in the vertical direction can be approximated as 12 times the extent of the depth [38]. Subsequent to the completion of vertical mixing, due to the effects of transverse dispersion and the variations in the transverse component of river velocity, contaminants achieve complete mixing in the transverse direction along the width of the river as well.

These processes are summarized as below and also represented in Figure 4.1:

- Mixing in the receiving water body will be 3-D at the discharge point and in the near vicinity of it (in vertical, transverse and longitudinal directions)
- It will be 2-D where vertical mixing is almost complete and transverse mixing becomes more significant (in transverse and longitudinal directions)
- It will be 1-D where complete mixing along the depth and width of the river is accomplished and at distances further away from the point of discharge (longitudinal direction, or the direction of flow)

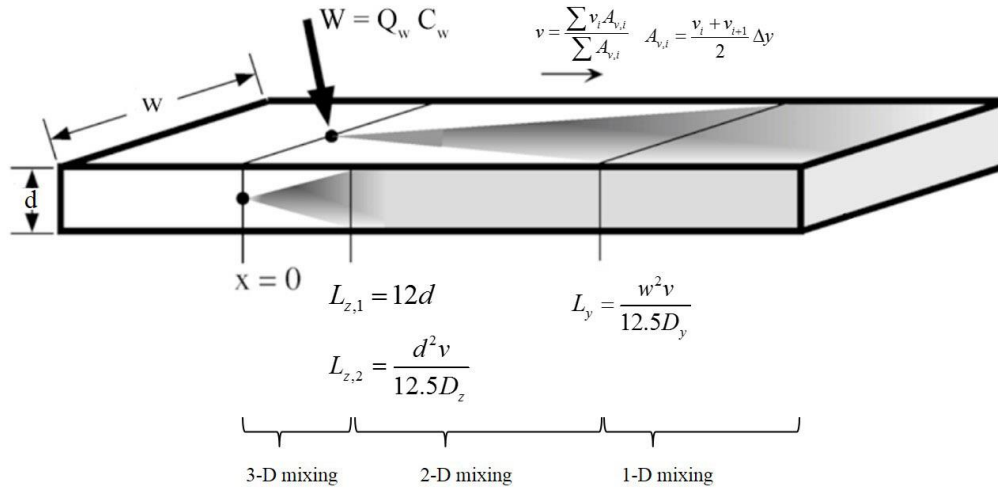


Figure 4.1. A depiction of the mixing processes that take place in river after an effluent discharge W is contaminant load in the effluent $[M/T]$, Q_w is the discharge flowrate $[L^3/T]$, C_w is the contaminant concentration in the discharge $[M/L^3]$, v is the receiving water body velocity $[L/T]$ (for the details about velocity calculations see Chapter 3), L_z is the vertical characteristic mixing distance $[L]$, i.e. the distance in the direction of the flow that complete mixing along the depth of the river is achieved, L_y is the transverse characteristic mixing distance $[L]$, i.e. the distance in the direction of flow that complete mixing along the width of the river accomplished, d is the depth of the river $[L]$, w is the width of the river $[L]$, D_z is the vertical dispersion coefficient $[L^2/T]$, and D_y is the transverse dispersion coefficient $[L^2/T]$.

More details about the mixing processes that take place in natural streams that are introduced above, and explanations about the novel discharge limit approach that is built upon these fundamental aspects are given in the following sections of this chapter.

4.1. Mass Transport Processes in Rivers

The movement of any substance which is added into a natural stream depends on many factors including density and temperature of river water, curvature of the river, any kind of non-uniformity in the river geometry including meanders, cavities, aquatic and riparian vegetation etc. [31], [38]–[42]. However, it is not practical taking all such details into consideration. Accordingly, mass transport in rivers is described under several main processes.

There are two major processes that affect on the transport of substances in rivers, namely, advection and dispersion.

4.1.1. Advection

In the context of natural streams, it is the name given to the movement of a mass by the influence of the current. The resultant velocity of the river in all directions creates the current and any substance that is introduced into this system follows it and moves in the direction of flow. Advective flux, J_{adv} , defined as “the amount of substance transported per unit time per unit area perpendicular to the current” [31], [39]–[41] is a concept to mathematically express and quantify advection and is given by:

$$J_{adv} = vC \quad (14)$$

where v is advective velocity [L/T] and C is the mass concentration of the substance [M/L³].

4.1.2. Molecular Diffusion

Molecular diffusion is a phenomenon that arises from the random motion of particles which results in a net movement of them from higher to lower concentration zones, concentration gradient being the driving force [31], [38]–[40]. This effect is mathematically described as a flux term by Fick’s first law and for 3-D is given as:

$$J_{dif} = -D \frac{\partial C}{\partial x} - D \frac{\partial C}{\partial y} - D \frac{\partial C}{\partial z} \quad (15)$$

where D is the molecular diffusion coefficient [L²/T] and x , y and z are the position vectors in longitudinal, transverse, and vertical directions, respectively.

Molecular diffusion has negligible influence on contaminant transport in river systems as compared to dispersion process to impact mixing under turbulent flow conditions. Since river flow is almost always turbulent, molecular diffusion is generally neglected [40].

4.1.3. Turbulent Diffusion

Basically, turbulence in fluids is related to mean velocity and viscosity. Random scattering of particles occur due to formation of eddies (secondary circulations) under turbulent flow conditions. This scattering creates an effect similar to molecular diffusion, but with a much larger magnitude. Thus, turbulent diffusion is also defined by a Fickian transport relationship and happens in all three dimensions, only with higher coefficients [39], [40].

4.1.4. Shear Dispersion

An influence called “shear” takes place as a result of irregularities in natural streams such as non-uniform river geometry, meandering, pools, riffles, bends etc. and natural phenomenon such as friction caused by wind and bed or bank of the stream. This shear causes gradients in all three directions of the velocity profile which in turn results in a mixing effect too complex to be modeled directly, however can also be approximated adequately by Fick’s first law of diffusion [39], [40].

4.1.5. Relationships for Dispersion Coefficients

Although molecular and turbulent diffusion and shear dispersion are caused by different mechanisms, their end results are mathematically expressed in identical fashion. Generally, the effect of molecular diffusion is negligible when compared to turbulent diffusion and shear dispersion for transport in rivers. And although turbulent diffusion and shear dispersion can be defined individually in theory, practically the two are not easily distinguishable. For example, Hemond and Fechner [6] argue that turbulence in rivers originate from shear which is related to the friction at the bottom and the sides. Therefore, the combined effects of the both are termed as “dispersion” and one coefficient for it is estimated for different directions commonly in the literature. However, the text aims to distinguish these two to the highest possible extent.

The following presents a brief summary based on an extensive literature survey for the relationships used to quantify dispersion coefficients.

As a result of the vertical velocity profile, it is argued that vertical shear dispersion coefficient varies parabolically with depth according to the following relationship [31], [41]:

$$\varepsilon_{K,z} = \kappa u^* \left(\frac{z}{d} \right) \left(1 - \frac{z}{d} \right) \quad (16)$$

where $\varepsilon_{K,z}$ is the local vertical shear dispersion coefficient [L^2/T], κ is the von Karman coefficient, d is channel depth [L], z is the vertical distance from the bottom of the channel [L], and u^* is the shear or friction velocity which is defined as the square root of the shear force exerted from the bottom and sides of a channel [6] and can be estimated as [6], [31], [38], [41], [43]:

$$u^* = \sqrt{gdS} \quad (17)$$

Here, g is the gravitational acceleration [L/T^2] and S is the channel slope [dimensionless].

The depth average of Elder's analysis gives the following relationship when κ is taken as 0.4 [31], [38], [41]:

$$K_z = 0.067 d u^* \quad (18)$$

where K_z is the vertical shear dispersion coefficient [L^2/T].

Fischer [44] builds further on Elder's analysis by combining it with Rozovskii's (as cited in [44]) transverse velocity profile in the presence of bends and therefore, secondary currents or eddies in a channel to obtain a relationship for shear dispersion:

$$K_y = -\frac{1}{\kappa^4} v^2 \frac{d^4}{r_c^2} \int_0^1 F\left(\frac{z}{d}\right) d\left(\frac{z}{d}\right) \int_0^{\frac{z}{d}} \frac{1}{\varepsilon_{K,z}} dz \int_0^{\frac{z}{d}} F\left(\frac{z}{d}\right) d\left(\frac{z}{d}\right) \quad (19-a)$$

and

$$F\left(\frac{z}{d}\right) = F_1\left(\frac{z}{d}\right) - \frac{1}{\kappa} \sqrt{\frac{f^*}{8}} F_2\left(\frac{z}{d}\right) \quad (19-b)$$

Here, K_y is the transverse shear dispersion coefficient [L^2/T], r_c is the radius of curvature [L], y is the transverse distance [L], w is the channel width [L], F_1 and F_2 are dimensionless functions (plots of which are given by Rozovskii (as cited in [44]), and f^* is the Darcy-Weisbach friction factor.

Above two expressions (equation 19) are further modified with the incorporation of radial velocity (u_r , equation 21) [44], [45]:

$$\frac{K_y}{du^*} = -\frac{I}{\kappa^5} \left(\frac{u_r}{u^*}\right)^2 \left(\frac{d}{r_c}\right)^2 \quad (20)$$

where I is the result of the above triple integral and u_r is the radial velocity [L/T] given by [44]:

$$u_r = -\frac{I}{\kappa^2} v \frac{d}{r_c} F\left(\frac{z}{d}\right) \quad (21)$$

These relationships however are not applicable in many cases because of the practical problems of obtaining local data for channels and natural streams. To overcome this problem, scientists have proposed semi-empirical or empirical relationships to generate dispersion coefficients using the limited hydraulic data available for rivers.

Fischer et al. [31] approximated the following empirical relationship for the transverse turbulent diffusion coefficient by utilizing the results of 75 separate experiments in straight, rectangular channels:

$$E_y = 0.15 du^* \quad (22)$$

where E_y is the transverse turbulent diffusion coefficient [L^2/T].

The same approximation is extended for a transverse dispersion coefficient that represents the combined effects of turbulent diffusion and shear dispersion for natural streams [31]:

$$\frac{D_y}{du^*} = 0.6 \pm 50\% \quad (23)$$

Similar to these findings, Deng et al. [46] used a set 138 experimental data collected by Rutherford (as cited in [46]) and came up with constant transverse turbulent diffusion coefficient.

$$\frac{E_y}{du^*} = 0.145 \quad (24)$$

Here, the resemblance of this factor with the value 0.15 given by Fischer et al. [31] is worth the mention.

A relationship for transverse shear dispersion coefficient is also given in the literature [46]:

$$\frac{K_y}{du^*} = \left(\frac{1}{3250} \right) \left(\frac{v}{u^*} \right) \left(\frac{w}{d} \right)^{1.38} \quad (25)$$

where K_y is the transverse shear dispersion coefficient [L^2/T].

These two relationships are combined in order to obtain an overall transverse dispersion coefficient that includes both the effects of turbulent diffusion and shear dispersion [46]:

$$D_y = E_y + K_y = \left[0.145 + \left(\frac{1}{3250} \right) \left(\frac{v}{u^*} \right) \left(\frac{w}{d} \right)^{1.38} \right] du^* \quad (26)$$

Transverse dispersion coefficients are not only important for the approximation of the extent of mixing zones, but also they can be utilized in estimating longitudinal dispersion coefficients.

Fischer et al. [31] have developed the following integral form for the longitudinal dispersion coefficient based upon the balance between advection and overall transverse dispersion (the combined effects of transverse turbulent diffusion and transverse shear dispersion):

$$D_x = -\frac{1}{A} \int_0^w u'(y) d(y) \int_0^y \frac{1}{\varepsilon_y(y) d(y)} \int_0^y d(y) u'(y) dy dy dy \quad (27)$$

In this equation, A is the cross-sectional area [L^2], $d(y)$ is the local depth [L], $\varepsilon_y(y)$ is the local transverse dispersion coefficient [L^2/T] and $u'(y)$ is defined as follows:

$$u'(y) = \bar{v}_z(y) - v \quad (28)$$

where $\bar{v}_z$ is local depth-averaged velocity [L/T].

Deng et al. [46] has simplified the suggested integral form (equation 27) by assuming symmetrical river geometry and making proper substitutions, thus obtained:

$$\frac{D_x}{du^*} = -\frac{\psi}{8D_y} \left(\frac{w}{d} \right)^2 \left(\frac{v}{u^*} \right)^2 I(\beta) \quad (29)$$

where ψ is a revision coefficient, which accounts for the deviations between smooth, laboratory channels and rough, natural streams and taken as 15 by Deng et al. [46] with a reference to Fischer et al.'s [31] findings on their experiments regarding longitudinal dispersion coefficient variations under different channel roughness conditions, and $I(\beta)$ is the result of the triple integration that can be seen in the integral form given in equation (27).

β is the channel shape parameter and is given by [45]:

$$\beta = \ln \left(\frac{w}{d} \right) \quad (30)$$

The dimensionless triple integral $I(\beta)$, as can be seen, is only dependent upon the width/depth ratio for a given natural stream, has also been simplified. It is numerically

integrated for 6 different w/d ratios which are typically seen in natural streams (10, 20, 30, 50, 100, 150, and 200) and with the results a regression equation was obtained as follows [46]:

$$I = -\frac{0.01}{(w/d)^{1/3}} \quad (31)$$

When this is substituted into the simplified form given in equation (29), a final relationship for the overall longitudinal dispersion coefficient is given as [46]:

$$D_x = \frac{0.15}{8D_y} \left(\frac{w}{d} \right)^{5/3} \left(\frac{v}{u^*} \right)^2 du^* \quad (32)$$

4.2. Estimation of Mixing Zones

A mixing zone is the region adjacent to the point of discharge which is of negligible size when compared to the whole length of a natural stream or its relevant reach, where the EQS can be exceeded for one or more substances [14]. This implies that, at the edge of this zone, the EQS level must be met [29]. Further definitions for mixing zones are generally left to the regional authorities since mixing is a phenomenon that depends highly on discharge and receiving water body conditions.

There are mainly two approaches for the estimation of the extent of mixing zones.

The first approach accepts the boundary of the mixing zone to be equal to the transverse characteristic mixing distance which as defined above signifies the longitudinal distance where complete mixing is achieved (in both vertical and transverse directions) and is calculated via empirical relations that are based upon a fundamental theory of dispersion (ToD-based empirical relations) (see 4.1.5. Relationships for Dispersion Coefficients). With the extent set, the analytical solutions of the advective-dispersive mass transport equation given in Table 4.1 are implemented to find out the maximum discharge concentration of the CoC that would yield a concentration equal to the EQS values at the end of the mixing zone, i.e. the discharge limit.

The second approach is similar to the first one, however it does not employ the aforementioned ToD-based empirical relations. Instead, in this approach, the analytical solutions of the mass transport equation (see Table 4.1) are further employed to estimate the characteristic mixing distances as well. Therefore, the longitudinal distances where the concentration gradient in the vertical and transverse directions are first determined by the multi-dimensional concentration profiles obtained from the analytical solutions. The transverse mixing distance denotes the extent of the mixing zone in the second approach as well. Yet, if this transverse mixing distance is to be accepted as the extent of a mixing zone, its magnitude should not be excessively large with respect to the overall length of the river or its tributary. This is usually examined by comparing the mixing distance with the width of the river at the point of discharge or with a generic limit value such as 1000 m which is suggested by the European Union as part of their mixing zone estimation guidelines [30]. The maximum CoC concentration in the discharge that would be dispersed enough to reach the EQS value at the end of this mixing zone is then estimated with the continued implementation of the analytical solutions of the mass transport equation.

Figure 4.2 also illustrates the extent of any mixing zone that is estimated by either one of the two approaches. Because of its description, a characteristic mixing distance is the distance in the direction of flow where complete mixing in a specific direction (vertical or transverse) is achieved. Although while using ToD-based empirical relations for their estimation, one does not actually check the concentration values, the hidden assumption is still that at the end of the estimated longitudinal distance the concentration gradients in the given direction are negligibly low.

The actual results of using analytical-solution-based and ToD-based mixing zones on discharge limits are discussed in more detail on the upcoming chapter.

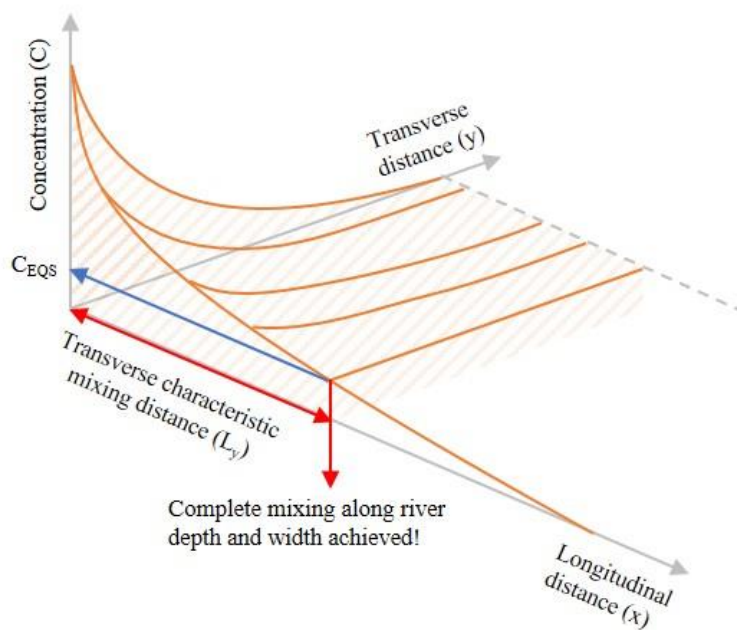


Figure 4.2. An illustration about the extent of mixing zones

The two approaches for the estimation of the extent of mixing zones explained above can be summarized as below:

- Estimation of vertical and transverse characteristic mixing distances using ToD-based empirical formulas and comparison of the EQS with the concentration values at that distance
- Estimation of the transverse characteristic mixing distance using relevant analytical solutions where the concentration of the substance is equal to the EQS value and examination of the acceptability of the size of this mixing distance as compared to either the overall length of the river or its tributary, the width of the river at the point of discharge or a generic limit value accepted by the authorities (e.g. 1000 m, mentioned by the EU)

4.3. Characteristic Mixing Distances

Due to the effect of dispersion in natural streams, although advection is dominantly in the direction of flow, the concentration of substances can get fully-mixed in the vertical and transverse directions.

For a point source discharge, the distance from the point of discharge that is travelled to reach complete-mixing in either vertical or transverse directions – where the effect of advection is negligible (assuming that river velocity has only one longitudinal component) and dispersion is the dominant process for mixing – is called the characteristic mixing distance.

Two approximations for the vertical characteristic mixing distances are given as follows [38]:

$$L_{z,1} = 12d \quad (33)$$

$$L_{z,2} = \frac{d^2 v}{12.5 K_z} \quad (34)$$

Due to the reason that among the relationships that are given for vertical characteristic mixing distance, $L_{z,1}$ is a gross approximation, for the rest of the text, $L_{z,2}$ will be used for the estimation of L_z values.

An approximation for the transverse characteristic mixing distance similar to the second expression above is also given as [38]:

$$L_y = \frac{w^2 v}{12.5 D_y} \quad (35)$$

Characteristic mixing distances are of significance for the study, since they are representative of the extent of mixing zones. Whether the extent should be taken as the vertical or the transverse characteristic mixing distance is to be answered according to the relative magnitude of each distance as compared to either river width or stream or reach length.

As the extent of the mixing zone, the EU suggests authorities to select the minimum between 10 times the river width at the point of discharge (similar to equation 33) or 1000 m [30].

4.4. Establishment of Discharge Limits

For the control of point source pollution, a “combined approach” is put forward in the WFD [14]. According to this approach, concentration restrictions on a point source discharge has to consider both technical achievability and the actual status of the river quality [47].

Best-available-techniques (BATs) a concept first introduced in 1996 by the EU’s Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC). It refers to the most environmentally efficient technologies and processes that are both economically and technically accessible. In the EU, technical information about BATs for various industrial sectors are compiled and distributed in BAT Reference Documents (BREFs) [12]. The best-available-techniques associated emission levels (BAT-AELs) or discharge standards are concentration or mass loading limits for given substances and sectors that are defined according to the BATs and are to be met at the end of pipe [47]. This indicates no relation to the exact conditions prevailing in the receiving water body.

To account for necessities of the receiving water body in order to maintain good water status, environmental quality standards (EQSs) are also designated. These EQSs are concentration limits for specific substances that are generated with regards to the health of human-beings or the ecosystem. In many cases according to the BATs, it would not be feasible to expect end-of-pipe concentrations that are less than or equal to the EQS values.

Therefore, with the combined approach, both BATs and the receiving water body health conditions are taken into account by the employment of the concept of mixing zones. Then, the question becomes whether a pollutant concentration at the end-of-

pipe (that is equal to or slightly above the BAT-AEL) will be lowered to the relevant EQS value by the forces of mixing at the end of the mixing zone, or not.

So, a discharge limit, that is a result of the combined approach, can be defined as the maximum end-of-pipe concentration of any substance which leads to non-exceedance of the relevant EQS value.

In order to estimate these discharge limits, river mixing models are employed. There have been several models proposed to date and it is not possible to claim that one fits for all cases. First and foremost, the requirements of each model are different and applicability of a model for any case is therefore highly dependent on the availability of data.

Baek and Seo [42], for the determination of certain mixing parameters (namely dispersion coefficients), mention two main categories of methods: observation and estimation. This information can be generalized for river mixing models. Some models rely upon tracer data which is either obtained through measurements done actually at the river or hydraulic experiments done in the laboratory where the river conditions are to be simulated.

The focus of this study will be on methods based on estimation, because they require less effort and therefore can be applied more widely. Estimation methods also vary in complexity and resolution which implies that there exists no one-size-fits-all solution. Each model has its own advantages and limitations and thus will be appropriate for certain conditions.

So far, much has been elucidated about the formation of mixing zones and the estimation of their extents in cases of pollutant discharge to rivers. Another important concept related to the mixing zone that needs more clarification is the discharge limit. A discharge limit, is the maximum permissible mass loading $[M/T]$ or concentration (mass loading/flowrate) $[M/L^3]$ for a given substance in a given discharge. Without the incorporation of the mixing zone concept, all discharge limits would be equal to the EQS values for the given discharges. Yet, as indicated previously, it is perfectly

reasonable to take the effects of transport (mixing) and/or transformation of substances into account, in order to render these limits more realistic.

For the relatively simplistic determination of a discharge limit for a substance that is contained in a given discharge, the variations of concentration of that substance along the depth, width and length of the stream has to be known. This involves the application of the following 3-dimensional advective-dispersive transport equation which is obtained by assuming that the vertical and transverse components of the advective velocity are negligible and dispersion/mixing coefficients are constant:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - v_x \frac{\partial C}{\partial x} + R \quad (36)$$

Here C is the concentration of a given substance [M/L³]; x, y and z are coordinates [L] and R represents the reactions that the substance is exposed to [M/L³/T].

This partial differential equation has analytical solutions under certain assumptions, initial and boundary conditions. The discharge is assumed to be continuous and point-source with constant pollutant load. The river bed and banks are assumed to be no-flux-boundaries. Receiving water body hydro-geometrics, hydrodynamic and mixing characteristics are assumed the same from the point of discharge to the end of the mixing zone. Differences in river hydro-geometry, and mixing conditions impose further modifications that lead to various analytical solutions that are either 1-, 2- or 3-D.

The variation of mentioned conditions in natural streams can be identified through the use of dimensionless coefficients such as Peclet, Pe, and Damkohler numbers, Da, as described by equations (37)-(39):

$$Pe = \frac{L_y v}{D_x} \quad (37)$$

$$Da^I = \frac{k L_y}{v} \quad (38)$$

$$Da^{II} = \frac{kL_y^2}{D_x} \quad (39)$$

where, Da^I is the advective Damkohler number, Da^{II} is the dispersive Damkohler number and k [1/T] is an exemplary first-order decay constant to represent the transformation term.

Peclet number (Pe) indicates whether advection or dispersion is more dominant in a given system. If $Pe \ll 1$ (i.e. $Pe \leq 0.1$), dispersion dominates advection and the system acts similar to a completely-mixed-flow-reactor, If $Pe \gg 1$ (i.e. $Pe \geq 10$) advection dominates dispersion and the system acts similar to a plug-flow-reactor. On the other hand, Damkohler number gives comparison between transport and transformation processes. If $Da \ll 1$ (i.e. $Da \leq 0.1$), transformation processes can be regarded negligible as compared to transport processes (either advection or dispersion). If $Da \gg 1$ (i.e. $Da \geq 10$), transport processes (either advection or dispersion) can be regarded as negligible as compared to transformation processes. Both processes are non-negligible and all processes must be taken into account for $0.1 < Pe/Da < 10$.

In all these dimensionless numbers, the characteristic mixing distance is taken as the distance from the point of discharge in the flow direction to where the substance is completely mixed in the transverse dimension, because as previously stated, complete mixing in the vertical direction for the most part occurs earlier than in the transverse direction due to depth being generally smaller than width in natural streams. This indicates that overall complete mixing is accomplished when river is completely mixed in the transverse direction.

Dispersion coefficient is taken as the longitudinal dispersion coefficient, since the mixing distance and advective velocity are both in the longitudinal direction as well.

Finally, 1-, 2- and 3-D analytical solutions are obtained according to the flow conditions determined by the dimensionless numbers. All cases that can be analytically solved according to the literature [31], [48], [49] are summarized in Table 4.1. The table is comprised of three main parts, two columns and 12 specific mixing

conditions. The main categorization of different conditions is based upon Peclet numbers, therefore three main parts are $Pe \ll 1$, $Pe \gg 1$ and $0.1 < Pe < 10$. Besides, on one side of the table additional conditions are given and on the other, the actual analytical solutions are provided along with a couple of steps of derivation.

Table 4.1. Analytical solutions of the advective-dispersive mass transport equation under different conditions

Conditions		Model equation and analytical solution	
Pe << 1			
<i>(advective transport is negligible as compared to longitudinal dispersive transport)</i>			
①	Generally not an applicable (valid) condition for rivers. In none of the monitored stations of Tersakan Creek or 73 data on rivers in the US collected from the literature [46], there is no reported Pe values less than 1.		
Pe >> 1			
<i>(longitudinal dispersive transport is negligible as compared to advective transport)</i>			
②	- Steady-state (time independent) - Continuous discharge - Da ≪ 1, first order decay with a constant k - Large L_y and L_z characteristic mixing distances (both horizontal and vertical dispersion cannot be neglected)	$D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} = v \frac{\partial C}{\partial x} + kC \quad (40)$ $C(x, y, z) = \frac{\exp\left(-\frac{kx}{v}\right) Q_w C_w}{4\pi x \sqrt{D_y D_z}} * \left[\sum_{n=-\infty}^{n=\infty} \exp\left(-\frac{v(y-2nw)^2}{4D_y x} - \frac{vz^2}{4D_z x}\right) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{n=\infty} \exp\left(-\frac{vy^2}{4D_y x} - \frac{v(z-2nd)^2}{4D_z x}\right) \right] \quad (41)$	Q_w is the discharge flowrate [L³/T], C_w is the discharge concentration of the pollutant. Image sources are at (x=0, y=-2nw, z=0) and (x=0, y=0, z=-2nd), real source is at (x=0, y=0, z=0).

Table 4.1. Analytical solutions of the advective-dispersive mass transport equation under different conditions (cont'd)

	Conditions	Model equation and analytical solution
3	- Steady-state (time independent) - Continuous discharge - Da << 1, decay negligible - Large L_y and L_z characteristic mixing distances	$D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} = v \frac{\partial C}{\partial x} \quad (42)$ $C(x, y, z) = \frac{Q_w C_w}{4\pi x \sqrt{D_y D_z}} * \left[\sum_{n=-\infty}^{\infty} \exp\left(-\frac{v(y-2nw)^2}{4D_y x} - \frac{vz^2}{4D_z x}\right) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \exp\left(-\frac{vy^2}{4D_y x} - \frac{v(z-2nd)^2}{4D_z x}\right) \right] \quad (43)$ Image sources are at (x=0, y=-2nw, z=0) ve (x=0, y=0, z=-2nd), real source is at (x=0, y=0, z=0).
4	- Steady-state (time independent) - Continuous discharge - Da <<< 1, first order decay with a constant k - Large L_y and small L_z characteristic mixing distances (vertical dispersion can, but transverse dispersion cannot be neglected, complete mixing along the depth at the point of discharge)	$D_y \frac{\partial^2 C}{\partial y^2} = v \frac{\partial C}{\partial x} + kC \quad (44)$ $C(x, y) = \frac{\exp\left(-\frac{kx}{v}\right) Q_w C_w}{vd \sqrt{4\pi D_y \frac{x}{v}}} * \sum_{n=-\infty}^{\infty} \exp\left(-\frac{v(y-2nw)^2}{4D_y x}\right) \quad (45)$ Image source is at (x=0, y=-2nw), real source is at (x=0, y=0).
5	- Steady-state (time independent) - Continuous discharge - Da << 1, decay negligible - Large L_y and small L_z characteristic mixing distances	$D_y \frac{\partial^2 C}{\partial y^2} = v \frac{\partial C}{\partial x} \quad (46)$ $C(x, y) = \frac{Q_w C_w}{vd \sqrt{4\pi D_y \frac{x}{v}}} * \sum_{n=-\infty}^{\infty} \exp\left(-\frac{v(y-2nw)^2}{4D_y x}\right) \quad (47)$ Image source is at (x=0, y=-2nw), real source is at (x=0, y=0).

Table 4.1. Analytical solutions of the advective-dispersive mass transport equation under different conditions (cont'd)

Conditions		Model equation and analytical solution	
6	- Steady-state (time independent) - Continuous discharge $Da \ll 1$, first order decay with a constant k - Small L_y and L_z characteristic mixing distances (both vertical and transverse dispersion can be neglected, complete mixing at the point of discharge)	$0 = v \frac{dC}{dx} + kC \tag{48}$ $C(x) = C_0 e^{-\frac{k}{v}x} \tag{49}$ $C_0 = \frac{Q_w C_w}{Q_r + Q_w} \tag{50}$ Q_r is the receiving body (river) flowrate [L^3/T].	
7	- Steady-state (time independent) - Continuous discharge $Da \ll 1$, decay negligible - Small L_y and L_z characteristic mixing distances	$0 = v \frac{dC}{dx} \tag{51}$ $Q_w C_w + Q_r C_r = (Q_w + Q_r) C_0 = Q C_0 \tag{52}$ $C_0 = \frac{Q_w C_w + Q_r C_r}{(Q_w + Q_r)} \tag{53}$ If $Q_r \gg Q_w$ & $C_r \ll C_w$ (54) $C_0 = \frac{Q_w C_w}{Q_w + Q_r} \tag{55}$ Only dilution is considered. C_0: concentration at the mixing zone (at the point of discharge)	
$0.1 \leq Pe \leq 10$			
<i>(both longitudinal dispersive transport and advective transport cannot be neglected)</i>			
8	- Steady-state (time independent) - Continuous discharge $Da \ll 1$, first order decay with a constant k - Small L_y and L_z characteristic mixing distances	$D_x \frac{d^2 C}{dx^2} = v \frac{dC}{dx} + kC \tag{56}$ $C(x) = C_0 \exp\left(\frac{vx}{2D_x} (1 \pm m)\right) \tag{57}$ (+ = upstream, - = downstream) $C_0 = \frac{Q_w C_w}{m(Q_w + Q_r)} \tag{58}$ $m = \sqrt{1 + \frac{4kD_x}{v^2}} \tag{59}$	

Table 4.1. Analytical solutions of the advective-dispersive mass transport equation under different conditions (cont'd)

	Conditions	Model equation and analytical solution
9	- Steady-state (time independent) - Continuous discharge - Da << 1, decay negligible - Small L_y and L_z characteristic mixing distances	$D_x \frac{d^2 C}{dx^2} = v \frac{dC}{dx} \quad (60)$ $C(x) = C_0 e^{\frac{vx}{D_x}} \text{ (upstream case)} \quad (61)$ $C = C_0 \text{ (downstream case)} \quad (62)$ $C_0 = \frac{Q_w C_w}{Q_w + Q_r} \quad (63)$
10	- Unsteady-state (time dependent) - Continuous discharge - Da <<< 1, first order decay with a constant k	$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - kC \quad (64)$ $C(x, t) = \frac{C_0}{2} \left[\exp\left(\frac{vx}{2D_x}(1 + \sqrt{1 + 2H})\right)^* \operatorname{erfc}\left(\frac{x + vt\sqrt{1 + 2H}}{\sqrt{4D_x t}}\right) + \exp\left(\frac{vx}{2D_x}(1 - \sqrt{1 + 2H})\right)^* \operatorname{erfc}\left(\frac{x - vt\sqrt{1 + 2H}}{\sqrt{4D_x t}}\right) \right] \quad (65)$ where, $H = \frac{2kD_x}{v^2} \quad (66)$
11	- Unsteady-state (time dependent) - Continuous discharge - Da << 1, decay negligible	$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (67)$ $C(x, t) = \frac{C_0}{2} \left[\exp\left(\frac{vx}{D_x}\right) \operatorname{erfc}\left(\frac{x + vt}{\sqrt{4D_x t}}\right) + \operatorname{erfc}\left(\frac{x - vt}{\sqrt{4D_x t}}\right) \right] \quad (68)$

Table 4.1. Analytical solutions of the advective-dispersive mass transport equation under different conditions (cont'd)

	Conditions	Model equation and analytical solution
12	Proper analytical solutions of the 2-D and 3-D mass transport equations are not available except for the above mentioned conditions (8-9). In such cases, software that builds on numerical solutions such as CORMIX etc. should be utilized. This implies that in these cases, modeling that relies on analytical solutions is insufficient, Tier 3 in the Tiered Approach suggested by the European Commission for the estimation of mixing zones and advanced numerical modeling should be employed.	

Figure 4.3 illustrates the approach developed in this chapter for the estimation of the extent of mixing zones and the establishment of discharge limits. The approach is based upon hydro-geometric and hydro-dynamic data. These data are taken as input to estimate river mixing parameters including dispersion coefficients, D_x (equation 32), D_y (equation 26), and K_z (equation 18), and characteristic mixing distances L_z (equation 34) and L_y (equation 35). These mixing parameters are then utilized in the calculation of dimensionless parameters Pe (equation 37) and Da (equations 38 and 39) for the identification of river mixing conditions. According to the values of Pe and Da , and other receiving water body and discharge conditions such as steadiness and continuity, the advective-diffusive mass transport equation (36) is modified or simplified, and relevant analytical solutions are obtained.

However, the attainment of mathematical expressions for analytical solutions is not the final step neither for the estimation of the extent of mixing zones, nor for the establishment of discharge limits.

As mentioned before, there are two approaches for mixing zone establishment. The extent of a mixing zone is either accepted as the transverse characteristic mixing distance (equation 35) or it is estimated utilizing the analytical solutions whenever possible (equations 41, 43, 45 and 47).

Then, the extent of the mixing zone and EQS for any given contaminant of concern (CoC) are employed in the relevant analytical solution in order to reach a maximum

discharge concentration that would not violate the EQS value at the end of the mixing zone.

To demonstrate the estimation of discharge limits, let a hypothetical discharge-receiving water body couple are under such conditions that the relevant analytical solution is equation 49, and therefore the extent of the mixing zone can only be determined by equation 34, i.e. an empirical relation that based upon a fundamental theory of dispersion.

$$C(x) = C_0 e^{-\frac{k}{v}x} \quad (49)$$

$$C(L_y) = C_{EQS} = \frac{Q_w C_w}{Q_r + Q_w} e^{-\frac{k}{v}L_y} \quad (69)$$

$$C_w = C_{DL} = C_{EQS} e^{\frac{k}{v}L_y} \frac{Q_r + Q_w}{Q_w} \quad (70)$$

It is also possible to estimate discharge limits for other analytical solutions. However it can be more tedious than the simple demonstration above. Especially, if the solution produces concentration values at different y and/or z distances, estimation of analytical-solution-based mixing distances and discharge limits becomes a trial-and-error process and therefore may require more complex computer programming where error minimization routines are involved.

Finally, the above explanations can be summarized as a step-wise approach for the determination of discharge limits as follows:

1. Dispersion coefficients, D_x , D_y , and D_z are estimated from river hydro-geometric and hydrodynamic data.
2. L_z , L_y , Pe , Da^I , and Da^{II} are obtained.
3. Using constraints that stem from L_z , L_y , Pe , Da^I , and Da^{II} , necessary modifications or simplifications are done and boundary conditions are set for the advective-dispersive mass transport equation (36).

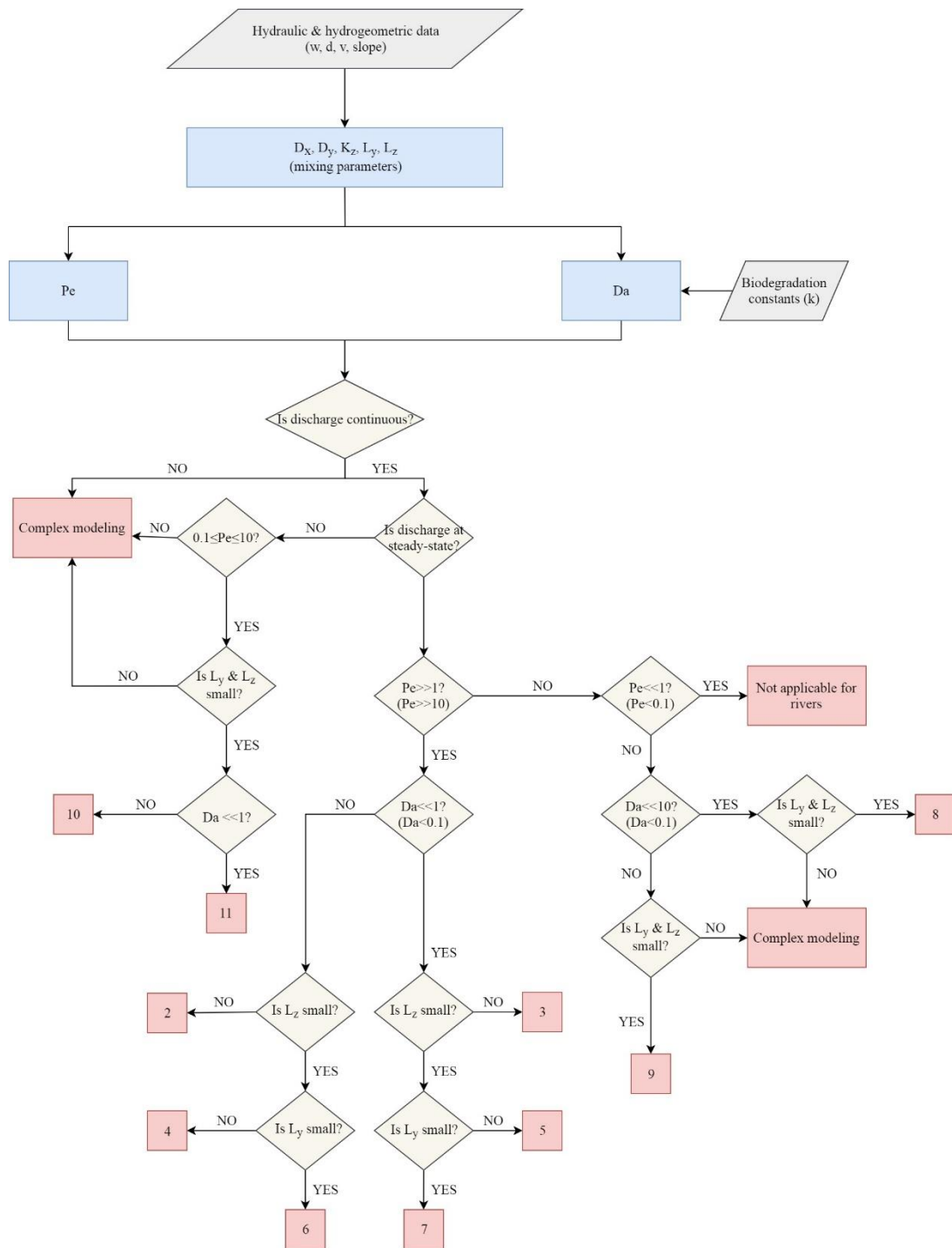


Figure 4.3. Flow diagram of the EQS-based discharge limit establishment approach developed

4. Analytical solution for the given modification of the advective-dispersive mass transport equation is obtained.
5. Discharge limit (permissible pollutant load) for the specific discharge point/mixing zone is estimated with the given analytical solutions and EQSs.

The approach that is summarized throughout this chapter is implemented as a MATLAB[®] program composed of a modular set of routines and sub-routines (see Appendix A for details). It is coded in MATLAB[®] 2018b running on a 64-bit Windows 10 operating system. MATLAB[®] built-in functions utilized in the code are carefully selected to prevent any compatibility issues and to provide convenience for any possible future adaption to other coding languages such as Python or JavaScript.

Upto this point, relevant literature has been reviewed in Chapter 2 and here, data to be utilized in the discharge limit estimation approach has been presented in Chapter 3, and the principles of the discharge limit estimation approach has been elucidated in this chapter. In the next chapter, finally, the results of the implementation of the approach for the suitable discharge cases within Tersakan sub-basin are presented and relevant discussions are made.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter begins with the discussion of the receiving water body hydro-dynamic and hydraulic data previously presented in Chapter 3 due their significance on the the discharge limit estimation approach. Then, the practical aspects of the discharge limit estimation approach that are specific to Tersakan sub-basin are explained and the results of the discharge limit establishment applications are presented and discussed. Later, a section about the estimation and significance of analytical-solution-based mixing distances follows. In the next couple of sections, relationships or correlations related to various parameters estimated for Tersakan sub-basin (including different mixing distances, discharge limits, Peclet numbers and river width to depth ratios) are discussed. Before some suggestions for further studies, the current status of water quality monitoring and its significance for the discharge limit estimation studies is briefly discussed.

5.1. Discussion on Hydro-geometric and Hydraulic Data from Tersakan Sub-Basin

For this study the variability in river water hydro-geometric and hydrodynamic parameters is significant because the novel approach developed here for the establishment of discharge limits, is comprised of mathematical models of river mixing that are based on these river characteristic information together with the discharge data.

Considering all monitoring stations and seasons, river width values change between 1.2-21.5 m, depth values vary between 8.00-76.5 cm, river cross-sectional areas are between 0.117-8.92 m², longitudinal velocities change between 0.095-1.01 m/s and river flowrates range between 0.014-6.26 m³/s.

As a result of the analysis of the monitoring data collected from receiving water body monitoring stations along Tersakan Creek, the high flowrate season for the sub-basin is determined as May to October, thus the low flowrate season becomes the period from November to April. This analysis is done by evaluating each receiving water body monitoring station individually by examining the months that the highest flowrates are observed.

Throughout Tersakan sub-basin, it is observed that river width/depth ratios and dimensionless Peclet numbers that are parameters that are informative of the receiving water body's hydro-geometric and mixing characteristics, do not have significant variations between high and low flowrate periods (for both parameters, the difference is around 0.5%).

For all receiving water body monitoring station data collected during 8 seasons:

- Longitudinal velocity (v) values in the high flowrate season are 10.5% greater and in the low flowrate season are 5.81% less than the average
- Width (w) values in the high flowrate season are 21.3% greater and in the low flowrate season are 11.8% less than the average
- Depth (d) values in the high flowrate season are 26.8% greater and in the low flowrate season are 14.9% less than the average
- Flowrate (Q) values in the high flowrate season are 61.3% greater and in the low flowrate season are 34.1% less than the average
- Shear velocity (u^*) values in the high flowrate season are 15.5% greater and in the low flowrate season are 8.61% less than the average
- Vertical characteristic mixing distance (L_z) values in the high flowrate season are 20.5% greater and in the low flowrate season are 11.4% less than the average
- Transverse characteristic mixing distance (L_y) values in the high flowrate season are 21.8% greater and in the low flowrate season are 12.1% less than the average

- Longitudinal dispersion coefficient (D_x) values in the high flowrate season are 32.1% greater and in the low flowrate season are 17.9% less than the average
- Transverse dispersion coefficient (D_y) values in the high flowrate season are 34.8% greater and in the low flowrate season are 19.4% less than the average
- Vertical dispersion coefficient (D_z) values in the high flowrate season are 40.0% greater and in the low flowrate season are 22.2% less than the average

A chart that represents the information given above is given in Figure 5.1.

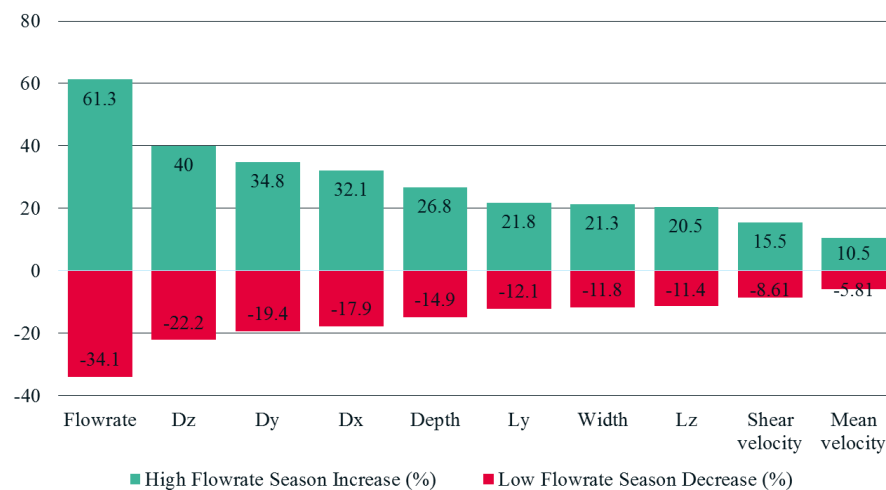


Figure 5.1. The percent increase and decrease of receiving water body hydro-geometric, hydrodynamic and mixing parameters according to high and low flowrate seasons as compared to the average values

These results indicate significant differences between river hydro-geometric, hydrodynamic and mixing characteristics in different seasons. Therefore, it would be important at least for discharges with mass loadings greater than or equal to 60-70% of the discharge limit (that seem permissible according to estimations based on average values), to consider the potential reduction of the discharge limits during low flowrate seasons.

5.2. Discharge Limit Establishment for Point Source Discharges in Tersakan Sub-Basin

EQS-based discharge limit establishment has been done for the 20 cases previously listed in Table 3.9 of Chapter 3, using the approach developed in Chapter 4 of this thesis.

The discharge limit (DL) establishment is done by the use of appropriate analytical solutions, selected according to the conditions listed in Table 4.1, and also illustrated as a flow diagram in Figure 4.3. As mentioned on the previous chapter, for the application of this approach MATLAB codes developed as part of the study are used (see Appendix A).

First and foremost, the receiving water body conditions prevailing at each of the 20 discharge cases that are suitable for discharge limit establishment applications within Tersakan sub-basin should be clearly identified so that the appropriate analytical solutions from Table 4.1 can be selected for further studies.

At the beginning, it should be reminded that these 20 cases are associated with only 4 receiving water body-discharge couples (see Table 3.3 and Table 3.9), so receiving water body hydro-geometric and mixing parameters will only be associated with the 4 relevant receiving water body stations. All relevant data for these 4 stations are given in Table 5.1. Besides, for both convenience and more conservative solutions, all the 20 cases will be assumed to have achieved steady-conditions (long term discharge), to have continuous discharges from the riverbank.

Table 5.1. *Relevant receiving water body hydro-geometric and mixing parameters associated with the four receiving water body monitoring stations that are suitable for discharge limit estimation applications*

No	Station ID	Station Name	Pe	d (m)	w (m)	w/d	L _z (m)	L _y (m)	L _y /L _z
1	YESIL-97	Merzifon OIZ	12	0.185	3.85	21	5.44E-01	9.47E+01	174
2	YESIL-109	Havza Municipal WWTP	15	0.264	11.10	42	2.88E+00	5.47E+02	190

Table 5.1. Relevant receiving water body hydro-geometric and mixing parameters associated with the four receiving water body monitoring stations that are suitable for discharge limit estimation applications (cont'd)

No	Station ID	Station Name	Pe	d (m)	w (m)	w/d	L _z (m)	L _y (m)	L _y /L _z
3	YESIL-125	Bakraç Dairy Products	14	0.268	10.00	37	1.31E+00	3.76E+02	287
4	YESIL-128	Amasya Sugar Factory	15	0.105	5.00	48	4.44E-01	1.91E+02	430

Pe: Peclet number; d: depth; w: width; L_z: vertical characteristic mixing distance, L_y: transverse characteristic mixing distance

From Table 5.1 it can be seen that Pe values are higher than 10 for all cases (between 12-15). River width/depth ratios are between 21 and 48, which indicate a difference between river width and depth greater than one order of magnitude, and L_y/L_z ratios change from 174 to 430 for the stations, that is a variation between L_y and L_z greater than two orders of magnitude. This investigation suggests that for all the receiving water body stations associated, the vertical dimension of the river (i.e. depth which is between 10.5-26.8 cm) is much smaller than the transverse dimension (i.e. width which is between 3.85-11.1 m). Therefore the conditions prevailing at the receiving water body stations that are suitable for discharge limit estimation studies are identical where advection dominates dispersion in the longitudinal direction ($Pe \gg 1$, or $Pe \geq 10$) and the river depth is negligibly small relative to the width, which leads to the 2-D analytical solution given with #5 (equation 47) in Table 4.1.

In order to arrive to discharge limits from these analytical solutions, the extents of the mixing zones should also be identified. Two methods to this end are introduced in Chapter 4 where the first one involves the direct adoption of characteristic mixing distances (L_z and L_y, vertical and transverse, respectively) estimated by empirical relations that are based on a theory of dispersion (E-ToD), and in the other approach, the longitudinal distance where the concentration is equal to the EQS can be found from the analytical solutions for discharges given the discharge concentration of the contaminant of concern.

The part of equation 47 that represents the imaginary sources (or the exponential sum part) is present for the estimation of concentrations along the transverse direction. Since the maximum concentration values along the river width are always seen on the riverbank (i.e. $y=0$ m) for a riverbank discharge, and the estimation of discharge limits involves the investigation of the extent of the mixing zone (i.e. the relatively small zone that is from the point of discharge to the longitudinal distance where the concentration of the contaminant of concern is equal to its environmental quality standard value, which can be observed from the riverbank, because any other concentration value at a given longitudinal distance along the transverse direction would be lower; see 4.2. Estimation of Mixing Zones for more detail), and thus riverbank concentration values, this “exponential sum part” can be ignored for discharge limit estimation applications. So, equation 47 becomes:

$$C(x) = \frac{Q_w C_w}{vd \sqrt{4\pi D_y \frac{x}{v}}} \quad (71)$$

where $C(x)$ is the riverbank concentration of the contaminant of concern (CoC) at longitudinal distance x [M/L^3], Q_w is the discharge flowrate [L^3/T], C_w is the discharge concentration of the CoC [M/L^3], v is the mean river velocity [L/T], d is the river depth [L], D_y is the transverse dispersion coefficient [L^2/T], and x is longitudinal distance from the point of discharge [L].

The equation is further arranged to have:

$$C(L_y) = C_{EQS} = \frac{Q_w C_{DL}}{vd \sqrt{4\pi D_y \frac{L_y}{v}}} \quad (72)$$

where L_y is the transverse characteristic mixing distance (an estimate for the extent of the mixing zone) [L], C_{EQS} is the environmental quality standard (EQS) value of the CoC [M/L^3], and C_{DL} is the discharge limit concentration for the CoC [M/L^3].

And therefore:

$$C_{DL} = \frac{C_{EQS} v d \sqrt{4\pi D_y \frac{L_y}{v}}}{Q_w} \quad (73)$$

Discharge limit values that are estimated using this relationship for all 20 discharge cases are presented on Table 5.2.

Other than discharge limits, discharge quotas (DQ) and discharge quota usage (DQU) percentages are given in Table 5.2. DQs are obtained by subtracting the upstream mass loading of CoCs from the discharge limit (in mass loading) for any case. And DQUs are the ratio between the actual discharge mass loadings to the DQs. Relevant relationships are given as follows:

$$DQ = W_{DL} - W_r = C_{DL} * Q_w - C_r * Q_r \quad (74)$$

$$DQU(\%) = \frac{W_w}{DQ} = \frac{C_w * Q_w}{C_{DL} * Q_w - C_r * Q_r} * 100 \quad (75)$$

According to these estimations, none of the 20 discharges violate discharge limits. Yet, some of them pose greater risk for the future.

3 out 20 of the discharges have DQU values greater than 50% (Merzifon OIZ-Tridecane, Merfizon OIZ-Ni, and Amasya Sugar Factory-Bis(2-ethylhexyl) terephthalate).

3 others out of the 17 rest have DQU values greater than 10% (Merzifon OIZ-NH₄-N, Merzifon OIZ-TP and Merzifon OIZ-Free CN).

6 of the remaining 14 have DQU values greater than 5% (Merzifon OIZ-Petroleum hydrocarbons, Merzifon OIZ-Ethylfluralin, Merzifon OIZ-TOC, Merzifon OIZ-Nonylphenol, Merzifon OIZ-COD, and Merzifon OIZ-Cd).

Table 5.2. Discharge limits, discharge quota usage percentages and other relevant information about the 20 discharge cases that are suitable for discharge limit estimation applications within Tersakan sub-basin

No	Station Name	Contaminant Name	EQS	C _w	Q _w (m ³ /s)	W _w (kg/d or ton/d)	C _r (µg/L or mg/L)	Q _r (m ³ /s)	W _r (kg/d or ton/d)	C _{DL} (µg/L or mg/L)	W _{DL} (kg/d or ton/d)	W _{DL} -W _r	W _w / (W _{DL} -W _r)
1	Merzifon OIZ	Tridecane (µg/L)	5.00E-02	1.48E+00	3.99E-03	5.10E-04	1.00E-02	5.96E-02	5.15E-05	2.32E+00	8.01E-04	7.50E-04	68.07%
2	Merzifon OIZ	Ni (µg/L)	4.00E+00	9.94E+01	3.99E-03	3.43E-02	1.47E+00	5.96E-02	7.56E-03	1.86E+02	6.41E-02	5.66E-02	60.66%
3	Amasya Sugar Factory	Bis(2-ethylhexyl) terephthalate (µg/L)	1.00E-01	1.15E+00	8.11E-03	8.09E-04	5.00E-04	6.91E-02	2.99E-06	1.94E+00	1.36E-03	1.35E-03	59.73%
4	Merzifon OIZ	NH ₄ -N (mg/L)	1.00E+00	2.19E+01	3.99E-03	7.56E-03	1.03E-01	5.96E-02	5.28E-04	4.65E+01	1.60E-02	1.55E-02	48.76%
5	Merzifon OIZ	TP (mg/L)	1.60E-01	1.94E+00	3.99E-03	6.68E-04	1.28E-01	5.96E-02	6.59E-04	7.43E+00	2.56E-03	1.91E-03	35.06%
6	Merzifon OIZ	Free CN (µg/L)	1.20E+00	9.54E+00	3.99E-03	3.29E-03	5.00E-01	5.96E-02	2.57E-03	5.58E+01	1.92E-02	1.67E-02	19.75%
7	Merzifon OIZ	Petroleum hydrocarbons (µg/L)	9.60E+01	3.02E+02	3.99E-03	1.04E-01	8.40E+01	5.96E-02	4.33E-01	4.46E+03	1.54E+00	1.11E+00	9.43%
8	Merzifon OIZ	Ethylfuralin (µg/L)	3.00E-01	1.09E+00	3.99E-03	3.78E-04	2.50E-03	5.96E-02	1.29E-05	1.39E+01	4.81E-03	4.80E-03	7.88%
9	Merzifon OIZ	TOC (mg/L)	8.00E+00	2.35E+01	3.99E-03	8.11E-03	2.09E+00	5.96E-02	1.07E-02	3.72E+02	1.28E-01	1.18E-01	6.90%
10	Merzifon OIZ	Nonylphenol (µg/L)	3.00E-01	7.61E-01	3.99E-03	2.62E-04	5.00E-04	5.96E-02	2.57E-06	1.39E+01	4.81E-03	4.81E-03	5.46%
11	Merzifon OIZ	COD (mg/L)	5.00E+01	1.14E+02	3.99E-03	3.95E-02	1.05E+01	5.96E-02	5.41E-02	2.32E+03	8.01E-01	7.47E-01	5.28%
12	Merzifon OIZ	Cd (µg/L)	8.00E-02	1.71E-01	3.99E-03	5.88E-05	2.95E-02	5.96E-02	1.52E-04	3.72E+00	1.28E-03	1.13E-03	5.20%
13	Merzifon OIZ	B (µg/L)	7.07E+02	1.28E+03	3.99E-03	4.41E-01	2.91E+02	5.96E-02	1.50E+00	3.28E+04	1.13E+01	9.83E+00	4.49%
14	Merzifon OIZ	Fenpropimorph (µg/L)	1.00E-01	1.45E-01	3.99E-03	5.01E-05	5.00E-02	5.96E-02	2.57E-04	4.65E+00	1.60E-03	1.35E-03	3.72%
15	Merzifon OIZ	Ti (µg/L)	2.60E+01	3.73E+01	3.99E-03	1.29E-02	3.84E+00	5.96E-02	1.97E-02	1.21E+03	4.17E-01	3.97E-01	3.24%
16	Merzifon OIZ	4-Chloroaniline (µg/L)	5.00E-03	6.30E-03	3.99E-03	2.17E-06	2.50E-03	5.96E-02	1.29E-05	2.32E-01	8.01E-05	6.73E-05	3.23%
17	Merzifon OIZ	Benz(a)pyrene (µg/L)	1.70E-04	2.00E-04	3.99E-03	6.90E-08	1.00E-04	5.96E-02	5.15E-07	7.90E-03	2.73E-06	2.21E-06	3.12%
18	Merzifon OIZ	Diphenyl ether; diphenyl oxide (µg/L)	6.00E+00	7.84E+00	3.99E-03	2.70E-03	5.00E-04	5.96E-02	2.57E-06	2.79E+02	9.62E-02	9.62E-02	2.81%
19	Havza Municipal WWTP	TOC (mg/L)	8.00E+00	9.83E+00	2.69E-02	2.29E-02	4.89E+00	1.28E+00	5.39E-01	7.18E+02	1.67E+00	1.13E+00	2.02%
20	Bakrac Dairy Products	TDS (mg/L)	1.50E+03	2.78E+03	8.87E-03	2.13E+00	1.36E+03	6.08E-01	7.15E+01	6.90E+05	5.29E+02	4.57E+02	0.47%

EQS: Environmental quality standard of the CoC; C_w: Discharge concentration of the CoC; Q_w: Discharge flowrate; W_w: Discharge mass loading of the CoC; C_r: River concentration of the CoC; Q_r: River flowrate; W_r: River mass loading of the CoC; C_{DL}: Discharge limit concentration of the CoC; W_{DL}: Discharge limit mass loading of the CoC

Another 7 of the 8 rest have DQU values greater than 1% (Merzifon OIZ-B, Merzifon OIZ-Fenpropimorph, Merzifon OIZ-4-Chloroaniline, Merzifon OIZ-Ti, Merzifon OIZ-Benzo(a)pyrene, Merzifon OIZ-Diphenyl ether; diphenyl oxide, and Havza Municipal WWTP-TDS).

Only one discharge (Bakraç Diary Products-TDS) has a DQU value below 1%.

If a DQU greater than 50% is regarded as very high, between 50-10% as high, between 10-5% as moderate, between 5-1% as low and less than 1% as very low future risk; 15% of the discharge cases investigated within Tersakan sub-basin will have very high future risk, 15% of them will pose high, 30% of them will have moderate, another 35% of them will be at low and 5% of them will possess very low future risk (see Figure 5.2).

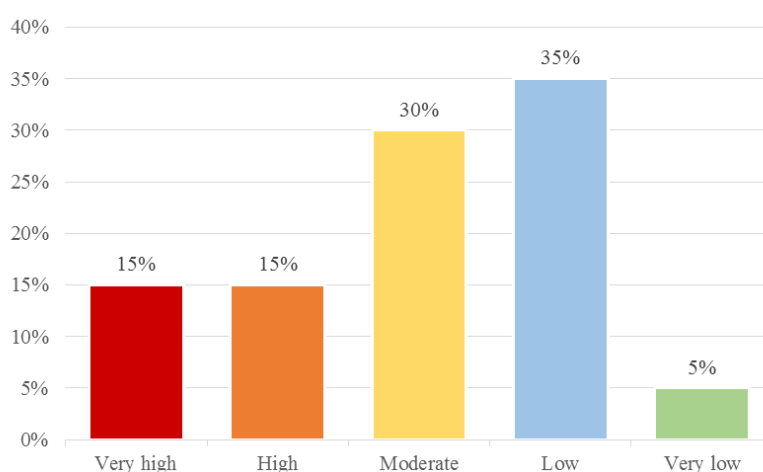


Figure 5.2. Future risk distributions associated with the 20 discharge cases within Tersakan sub-basin [Very high: Discharge Quota Used (DQU) $\geq 50\%$; High: $50\% \geq \text{DQU} \geq 10\%$; Moderate: $10\% \geq \text{DQU} \geq 5\%$; Low: $5\% \geq \text{DQU} \geq 1\%$; Very low: $1\% \geq \text{DQU}$ (DQU values for all 20 discharges within Tersakan sub-basin are found in Table 5.2)]

Among the discharge cases shown in Table 5.2, the third one, which appears as one of the most significant discharges within Tersakan sub-basin, due to being monitored for only one season may not reflect the actual case prevailing at the discharge point and thus may not be a reliable result. All other discharges are monitored for at least two seasons. For more details see Table 3.3.

Another important point to remember from the previous section of this chapter is that receiving water body hydro-geometric and hydrodynamic parameters occur to have significant variations between low and high flowrate seasons. Therefore, at least the discharges that have very high future risk, may already be exceeding the EQS value during low flowrate seasons. To check the situation of our 20 cases, the monitoring periods available for the 4 distinct receiving water body monitoring stations are examined and the results are as below:

- Merzifon OIZ (YESIL-97): 2 seasons of available monitoring data (2/2 low flowrate season)
- Amasya Sugar Factory (YESIL-128): 1 season of available monitoring data (1/1 low flowrate season)
- Bakraç Diary Products (YESIL-125): 2 seasons of available monitoring data (2/2 low flowrate season)
- Havza Municipal WWTP (YESIL-109): 3 seasons of available monitoring data (2/3 low flowrate season)

It appears that the data used in the discharge limit applications originate predominantly from low flowrate season monitoring results. This indicates that the results are on the more conservative side. It is critical to note that relevant data for all the three discharges that are categorized as very high future risk, originate completely from low flowrate season monitoring results.

Among the discharge cases shown in Table 5.2, the third one, which appears as one of the most significant discharges within Tersakan sub-basin, due to being monitored for only one season may not reflect the actual case prevailing at the discharge point and thus may not be a credible result. All other discharges are monitored for at least two seasons. For more details see Table 3.3.

Five of these CoCs discharged from Merzifon OIZ also have discharge standards set according to industrial conditions of mixed industrial WWTPs in the Water Pollution Control Regulation of the Ministry of Environment and Urbanization of the Republic

of Turkey (see Table 5.3 for a full list of all regulated parameters). As can be seen from Table 5.4, $\text{NH}_4\text{-N}$ and TP concentrations of the discharge violate the end-of-pipe limits (since TKN parameter counts both for organic-N and $\text{NH}_4\text{-N}$), whereas COD and Cd parameters are not violated. Yet, it is not possible to make a certain distinction about the CN^- parameter, since different CN^- species may be present other than free CN^- .

Table 5.3. *End-of-pipe discharge standards set for mixed industrial WWTPs taken from the Water Pollution Control Regulation of Ministry of Environment and Urbanization of the Republic of Turkey (Table 19 in the regulation's appendix) [27]*

Parameter	Composite Sample (2 h)	Composite Sample (24 h)	Minimum
COD (mg/L)	400	300	300
TSS (mg/L)	200	100	100
Oil and grease (mg/L)	20	10	10
TP (mg/L)	2	1	1
Total Cr (mg/L)	2	1	1
Cr^{6+} (mg/L)	0.5	0.5	0.5
Pb (mg/L)	2	1	1
Total CN^- (mg/L)	1	0.5	0.5
Cd (mg/L)	0.1	-	0.1
Fe (mg/L)	10	-	10
F^- (mg/L)	15	-	15
Cu (mg/L)	3	-	3
Zn (mg/L)	5	-	5
Hg (mg/L)	-	0.05	0.05
SO_4^{2-} (mg/L)	1500	1500	1500
TKN (mg/L)	20	15	15
Fish Bioanalysis (TDF)	10	10	10
pH	6-9	6-9	0
Color (Pt-Co)	280	260	260

Table 5.4. *Part of all 20 discharges within Tersakan sub basin that have end-of-pipe discharge standards set in the Turkish Water Pollution Control Regulation with their discharge concentrations, relevant end-of-pipe discharge standard values and violation status*

Station	Parameter	Discharge conc.	Discharge standard	Violation?
Merzifon OIZ	NH₄-N (mg/L)	2.19E+01	<15	Yes
Merzifon OIZ	TP (mg/L)	1.94E+00	1	Yes
Merzifon OIZ	Free CN (µg/L)	9.54E+00	<500	No?
Merzifon OIZ	COD (mg/L)	1.14E+02	300	No
Merzifon OIZ	Cd (µg/L)	1.71E-01	100	No

Under these conditions, although none of the discharges violate the newly established discharge limits, careful attention should still be given to very high and high future risk discharges (30% of all investigated, see Figure 5.2) and measures should also be taken to reduce NH₄-N and TP parameters since they seem to violate the end-of-pipe technology-based standards given in environmental legislation.

On a separate note, since for all the discharges suitable for the use of discharge limit estimation approach Peclet numbers calculated at the receiving water body monitoring stations are as greater than 10, at none of them more complex mixing is necessary and the application of the novel approach was suitable for all.

Yet, because all four discrete discharge points (Merzifon OIZ, Havza Municipal WWTP, Bakraç Dairy Products, and Amasya Sugar Factory) have similar mixing characteristics, all solutions included in the discharge limit estimation approach could not be tested via the case study. Another particular reason for this situation is that Tersakan sub-basin has already been subjected to high pollution loads. Many of the monitored parameters have receiving water body concentrations above the EQS level at present and therefore these parameters have to be immediately excluded from discharge limit estimation applications. One suitable receiving water body-discharge station couple needed to be ruled out from the study due to this reason (ET-BİR Suluova Slaughterhouse).

Thus, it can be said that the case study has only been partly successful in terms of inclusion of diverse cases that span the whole workspace of the discharge limit establishment approach.

However, this does not invalidate that the approach is able to combine simplicity (relative to more complex models such as CORMIX, Plumes etc.) and a level of scrutiny by the utilization of analytical solutions which allows less data requirement on one hand, and integrating many of such solutions to be used according the specific conditions prevailing at different discharge points. This also renders the method sensitive to the alterations either at the receiving water body or the discharge.

5.3. Estimation of Analytical-Solution-Based Mixing Distances

It has been explained in Chapter 4 that the extent of mixing zones can be estimated according two approaches. One, involves the direct adoption of characteristic mixing distances that are estimated via empirical relations that are based upon a fundamental theory of dispersion (E-ToD). The second approach is to employ the analytical solutions to find the mixing distances where the concentration of a particular discharge becomes equal to its EQS value.

The first approach is implemented in the previous section while the discharge limits are being estimated. The second approach is examined in a separate section because it does not generate discharge limits per se, yet it still produces analytical-solution-based (ASB) mixing distances, which also have proven to be a useful piece of information.

Therefore, the aims of this section are to investigate the implications of the 2-D analytical solution (equation 47), to comment on the concentration profiles obtained from it, to compare the results collected from it (which are more exact in nature), with the results got from the empirical relations, and to discuss about each method's (analytical and empirical) own objectives and fields of operation.

First of all, the second approach for the estimation of ASB mixing distances is also coded in MATLAB as a computer program (see Appendix A for the details), similar to the first one.

The program runs under a definite discharge concentration and a first guess for the distance. This guessed value has to be greater than the ASB mixing distance to be estimated, so the procedure has an iterative nature. The resulting ASB mixing distance is read from a line graph that is composed of two lines. One of them is the estimated concentration values of the CoC in the river vs. the longitudinal distance at the river bank ($y=0$ m) line and the other is a straight line that shows the relevant EQS for the CoC. The point where these two lines intersect is the ASB mixing distance. Since the system is assumed to be 2-D, concentration distributions do not change along the vertical direction.

An example of this procedure is given for the most significant discharge among the 20 cases within Tersakan sub-basin determined in the previous section which is the tridecane discharge from Merzifon OIZ. Mean discharge concentration of tridecane is monitored as $1.48 \mu\text{g/L}$, whereas the EQS value that should be observed at the receiving water body is $0.05 \mu\text{g/L}$. Initial guess for the longitudinal discharge is first taken as 20 m.

It can be seen from Figure 5.3 that the EQS and CoC concentration lines do not intersect at any point. Therefore, the initial guess is increased to 100 m.

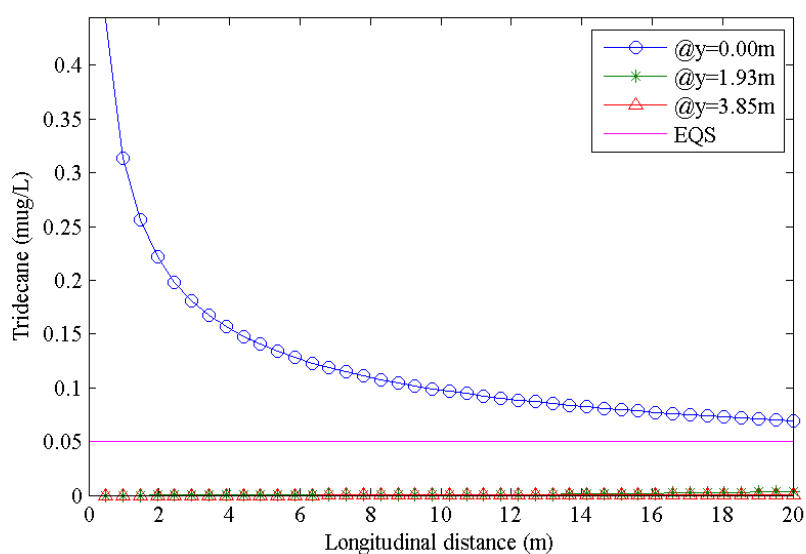


Figure 5.3. Tridecane concentration vs. Longitudinal distance graph with initial longitudinal distance guess equal to 20 m for Merzifon OIZ discharge

The point of intersection of the tridecane concentration in the river and the EQS lines is now visible in Figure 5.4. The distance in x-direction corresponding to this intersection point is around 40 m. So, the last run will be with a guess of longitudinal distance equal to 50 m.

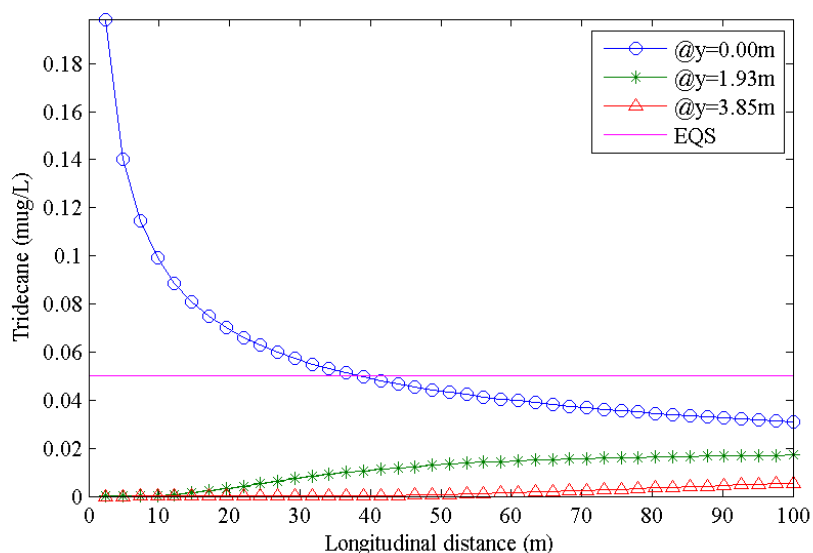


Figure 5.4. Tridecane concentration vs. Longitudinal distance graph with initial longitudinal distance guess equal to 100 m for Merzifon OIZ discharge

From Figure 5.5 the intersection point can be read as 38.5 m and this is indeed the ASB mixing zone.

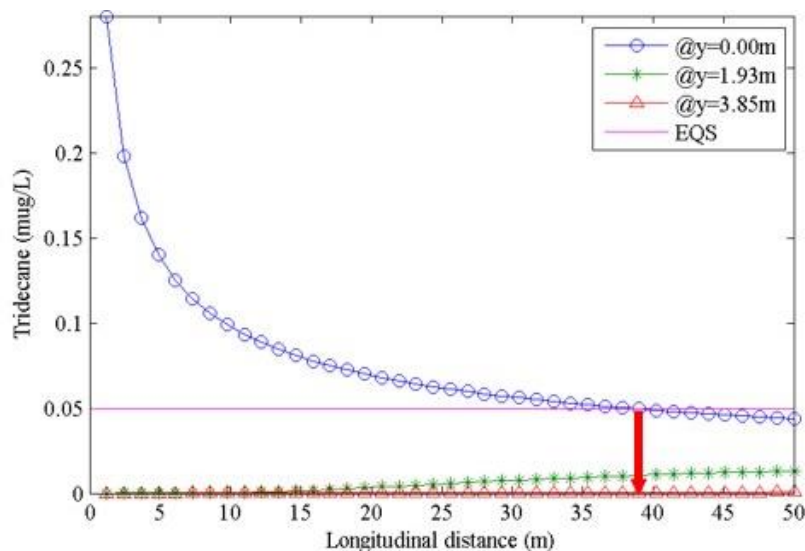


Figure 5.5. Tridecane concentration vs. Longitudinal distance graph with initial longitudinal distance guess equal to 50 m for Merzifon OIZ discharge (The arrow shows the longitudinal extent of the ASB mixing zone)

Additional observations can also be made from Figure 5.5 and Figure 5.6. First of all, in Figure 5.5 it can be seen that the transverse extent of the mixing zone is very limited since the concentrations at $y = 1.93$ m and $y = 3.85$ m are much below the EQS value throughout the longitudinal distance. Figure 5.6 verifies this as well, with a transverse tridecane concentration profile decreasing below the EQS level around $y = 0.4$ m and $y = 0.6$ m for $x = 1.22$ m and $x = 25.61$ m respectively, and below the EQS level throughout at $x=50$ m. Considering that the mean width of the river at the Merzifon OIZ discharge point is equal to 3.85 m, the maximum transverse extent observable from the Figure 5.6 (0.6 m) corresponds to 16% of the overall width of the river.

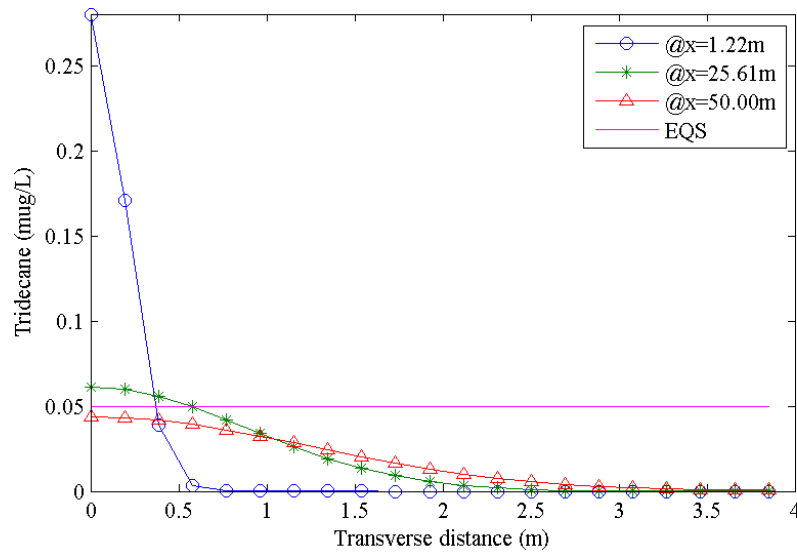


Figure 5.6. Tridecane concentration vs. transverse distance with initial longitudinal distance guess equal to 50 m for Merzifon OIZ discharge

Before moving on, it should be noted that all these observations are discharge-specific, which means they are not generalized realities involving the whole sub-basin. The aim in such discussion is to demonstrate the diversity of information that can be generated via the approach developed.

5.4. Relationships Related to Mixing Distances

In Table 5.5 the ASB and E-ToD mixing distances ($L_{y,ASB}$ and $L_{y,E-ToD}$) and their ratios together with the CoC concentration values associated with them, receiving water body CoC concentrations (C_w) and CoC discharge limit concentrations (C_{DL}) respectively and their ratios are given for all 20 specific cases within Tersakan sub-basin.

An immediate observation from Table 5.5 is that the E-ToD mixing distances are greater than the ASB mixing distances in all cases. This is since the ASB mixing distances result from an exact solution, in the estimation process the whole river width is not necessarily considered, i.e. the solution stops where the receiving water body concentration of the CoC decreases below its EQS value. However, the empirical

relations implemented in the estimation of the E-TOD mixing distances are developed to account for the condition where the concentration across the river width is completely mixed.

Table 5.5. ASB and E-ToD mixing distances ($L_{y,ASB}$ and $L_{y,E-ToD}$) and their ratios, with the CoC concentration values associated with them, river CoC concentrations (C_w) and CoC discharge limit concentrations (C_{DL}) respectively and their ratios for all 20 specific cases within Tersakan sub-basin

No	Station Name	Contaminant Name	$L_{y,ASB}$ (m)	$L_{y,E-ToD}$ (m)	$L_{y,E-ToD} / L_{y,ASB}$	C_w	C_{DL}	C_{DL} / C_w
1	Merzifon OIZ	Tridecane ($\mu\text{g/L}$)	3.84E+01	9.47E+01	2.46E+00	1.48E+00	2.32E+00	1.57E+00
2	Merzifon OIZ	Ni ($\mu\text{g/L}$)	2.71E+01	9.47E+01	3.49E+00	9.94E+01	1.86E+02	1.87E+00
3	Amasya Sugar Factory	Bis(2-ethylhexyl) terephthalate ($\mu\text{g/L}$)	6.79E+01	1.91E+02	2.81E+00	1.15E+00	1.94E+00	1.68E+00
4	Merzifon OIZ	$\text{NH}_4\text{-N}$ (mg/L)	2.11E+01	9.47E+01	4.50E+00	2.19E+01	4.65E+01	2.12E+00
5	Merzifon OIZ	TP (mg/L)	6.43E+00	9.47E+01	1.47E+01	1.94E+00	7.43E+00	3.84E+00
6	Merzifon OIZ	Free CN ($\mu\text{g/L}$)	2.77E+00	9.47E+01	3.42E+01	9.54E+00	5.58E+01	5.85E+00
7	Merzifon OIZ	Petroleum hydrocarbons ($\mu\text{g/L}$)	4.35E-01	9.47E+01	2.18E+02	3.02E+02	4.46E+03	1.48E+01
8	Merzifon OIZ	Ethylfluralin ($\mu\text{g/L}$)	5.84E-01	9.47E+01	1.62E+02	1.09E+00	1.39E+01	1.27E+01
9	Merzifon OIZ	TOC (mg/L)	3.78E-01	9.47E+01	2.50E+02	2.35E+01	3.72E+02	1.58E+01
10	Merzifon OIZ	Nonylphenol ($\mu\text{g/L}$)	2.82E-01	9.47E+01	3.36E+02	7.61E-01	1.39E+01	1.83E+01
11	Merzifon OIZ	COD (mg/L)	2.30E-01	9.47E+01	4.12E+02	1.14E+02	2.32E+03	2.03E+01
12	Merzifon OIZ	Cd ($\mu\text{g/L}$)	1.99E-01	9.47E+01	4.75E+02	1.71E-01	3.72E+00	2.18E+01
13	Merzifon OIZ	B ($\mu\text{g/L}$)	1.44E-01	9.47E+01	6.59E+02	1.28E+03	3.28E+04	2.57E+01
14	Merzifon OIZ	Fenpropimorph ($\mu\text{g/L}$)	9.24E-02	9.47E+01	1.03E+03	1.45E-01	4.65E+00	3.20E+01
15	Merzifon OIZ	Ti ($\mu\text{g/L}$)	9.04E-02	9.47E+01	1.05E+03	3.73E+01	1.21E+03	3.24E+01
16	Merzifon OIZ	4-Chloroaniline ($\mu\text{g/L}$)	6.97E-02	9.47E+01	1.36E+03	6.30E-03	2.32E-01	3.69E+01
17	Merzifon OIZ	Benzo(a)pyrene ($\mu\text{g/L}$)	6.07E-02	9.47E+01	1.56E+03	2.00E-04	7.90E-03	3.95E+01
18	Merzifon OIZ	Diphenyl ether; diphenyl oxide ($\mu\text{g/L}$)	7.48E-02	9.47E+01	1.27E+03	7.84E+00	2.79E+02	3.56E+01
19	Havza Municipal WWTP	TOC (mg/L)	1.03E-01	5.47E+02	5.33E+03	9.83E+00	7.18E+02	7.30E+01

Table 5.5. ASB and E-ToD mixing distances ($L_{y,ASB}$ and $L_{y,E-ToD}$) and their ratios, with the CoC concentration values associated with them, river CoC concentrations (C_w) and CoC discharge limit concentrations (C_{DL}) respectively and their ratios for all 20 specific cases within Tersakan sub-basin (cont'd)

No	Station Name	Contaminant Name	$L_{y,ASB}$ (m)	$L_{y,E-ToD}$ (m)	$L_{y,E-ToD} / L_{y,ASB}$	C_w	C_{DL}	C_{DL} / C_w
20	Bakrac Dairy Products	TDS (mg/L)	6.10E-03	3.76E+02	6.16E+04	2.78E+03	6.90E+05	2.48E+02

The ratios for mixing distances (E-ToD to ASB) range between 2.47 and 61,600 which shows an underestimation of the mixing distances for all cases. Considering the conclusions of the previous section where all discharges resulted to be permissible (i.e. discharge limits are estimated to be greater than the discharge loads of the CoCs) and that the ASB mixing distances are not independent from discharge mass loadings of the CoCs, it can be generalized for the 2-D analytical solution (equation 47) that for discharges with CoC mass loadings that conform with the discharge limits estimated, the ASB mixing distances are less than E-ToD mixing distances.

Although it does not lead to the generation of alternative discharge limits, the ASB mixing distance estimated here can as well be useful for point-source pollution control in rivers. For a discharge that is permissible according to the discharge limits previously estimated by the utilization of E-ToD mixing distances, without the consideration of ASB mixing distances, the extent of a mixing zone (i.e. the longitudinal distance from the point of discharge to the point where the CoC concentration is just below the EQS value) would be fixed at the E-ToD mixing distance value, which has a greater value than its ASB counterpart, and thus would imply a more strict restriction for another discharge of the same CoC to the river. However, with the incorporation of the ASB mixing distance to the decision mechanism, the mixing zone can be reduced and a second discharge of the same CoC can be made at a point that is less distant from the first point of discharge relative to the E-ToD mixing distance.

The correlation between these ratios are investigated on Figure 5.7. The ratios of mixing distances (R_{Ly}) seem to correlate perfectly ($R^2 = 1$) with the ratios of CoC concentrations (R_C) according to a power function relation almost equal to:

$$R_{Ly} = R_C^2 \quad (76)$$

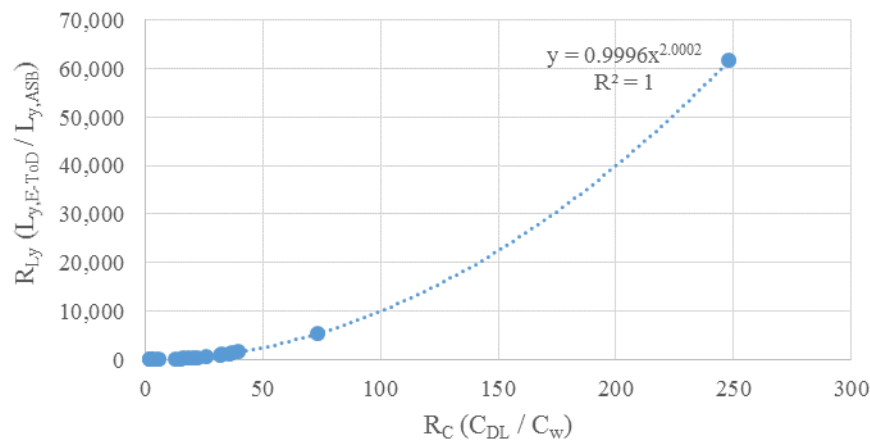


Figure 5.7. R_{Ly} (ratios of mixing distances) vs. R_C (ratios of CoC concentrations)

Further, the E-ToD and ASB mixing distances estimated as part of the study can be compared with the ballpark mixing distances estimated through the use of the simple approach proposed by the European Union. The relation is given as 10 time the river width at the particular receiving water body station as stated in Chapter 2 as well. The values for E-ToD and ASB mixing distances and river width and 10*width for 20 discharge cases in Tersakan sub-basin are given in Table 5.6.

Table 5.6. ASB, E-ToD mixing distances ($L_{y,ASB}$ and $L_{y,E-ToD}$), river width (w), $10 * \text{river width}$, and ratios for $10*w$ per ASB and E-ToD mixing distances

No	Station Name	Contaminant Name	$L_{y,ASB}$ (m)	$L_{y,E-ToD}$ (m)	w (m)	$10*w$ (m)	$10*w / L_{y,ASB}$	$10*w / L_{y,E-ToD}$
1	Merzifon OIZ	Tridecane ($\mu\text{g/L}$)	3.84E+01	9.47E+01	3.85	38.5	1.00E+00	4.06E-01
2	Merzifon OIZ	Ni ($\mu\text{g/L}$)	2.71E+01	9.47E+01	3.85	38.5	1.42E+00	4.06E-01
3	Amasya Sugar Factory	Bis(2-ethylhexyl) terephthalate ($\mu\text{g/L}$)	6.79E+01	1.91E+02	5	50	7.36E-01	2.62E-01
4	Merzifon OIZ	NH ₄ -N (mg/L)	2.11E+01	9.47E+01	3.85	38.5	1.83E+00	4.06E-01
5	Merzifon OIZ	TP (mg/L)	6.43E+00	9.47E+01	3.85	38.5	5.99E+00	4.06E-01
6	Merzifon OIZ	Free CN ($\mu\text{g/L}$)	2.77E+00	9.47E+01	3.85	38.5	1.39E+01	4.06E-01
7	Merzifon OIZ	Petroleum hydrocarbons ($\mu\text{g/L}$)	4.35E-01	9.47E+01	3.85	38.5	8.85E+01	4.06E-01
8	Merzifon OIZ	Ethylfluralin ($\mu\text{g/L}$)	5.84E-01	9.47E+01	3.85	38.5	6.59E+01	4.06E-01
9	Merzifon OIZ	TOC (mg/L)	3.78E-01	9.47E+01	3.85	38.5	1.02E+02	4.06E-01
10	Merzifon OIZ	Nonylphenol ($\mu\text{g/L}$)	2.82E-01	9.47E+01	3.85	38.5	1.36E+02	4.06E-01
11	Merzifon OIZ	COD (mg/L)	2.30E-01	9.47E+01	3.85	38.5	1.68E+02	4.06E-01
12	Merzifon OIZ	Cd ($\mu\text{g/L}$)	1.99E-01	9.47E+01	3.85	38.5	1.93E+02	4.06E-01
13	Merzifon OIZ	B ($\mu\text{g/L}$)	1.44E-01	9.47E+01	3.85	38.5	2.68E+02	4.06E-01
14	Merzifon OIZ	Fenpropimorph ($\mu\text{g/L}$)	9.24E-02	9.47E+01	3.85	38.5	4.17E+02	4.06E-01
15	Merzifon OIZ	Ti ($\mu\text{g/L}$)	9.04E-02	9.47E+01	3.85	38.5	4.26E+02	4.06E-01
16	Merzifon OIZ	4-Chloroaniline ($\mu\text{g/L}$)	6.97E-02	9.47E+01	3.85	38.5	5.53E+02	4.06E-01
17	Merzifon OIZ	Benzo(a)pyrene ($\mu\text{g/L}$)	6.07E-02	9.47E+01	3.85	38.5	6.34E+02	4.06E-01
18	Merzifon OIZ	Diphenyl ether; diphenyl oxide ($\mu\text{g/L}$)	7.48E-02	9.47E+01	3.85	38.5	5.14E+02	4.06E-01
19	Havza Municipal WWTP	TOC (mg/L)	1.03E-01	5.47E+02	11.1	111	1.08E+03	2.03E-01
20	Bakrac Dairy Products	TDS (mg/L)	6.10E-03	3.76E+02	10.0	100	1.64E+04	2.66E-01

As can be viewed from Table 5.6 the $10 * \text{width}$ values range from 0.203 to 0.406 times the E-ToD mixing distance values and from 0.736 to 16,300 times the ASB mixing distance values. So, $10 * \text{width}$ approximation underestimates the E-ToD mixing distances in all cases, and mostly overestimates (except for 1 in 20) the ASB mixing distances. Since ASB mixing distances depend on discharge loads of the CoCs,

they seem to have no interrelationship. However, since both are based on hydro-geometric and hydrodynamic parameters of the receiving water body, $10 * \text{width}$ values and E-ToD mixing distances may show correlation. The two are plotted against each other on Figure 5.8 and there occurs to be a linear correlation with an $R^2 = 0.9723$.

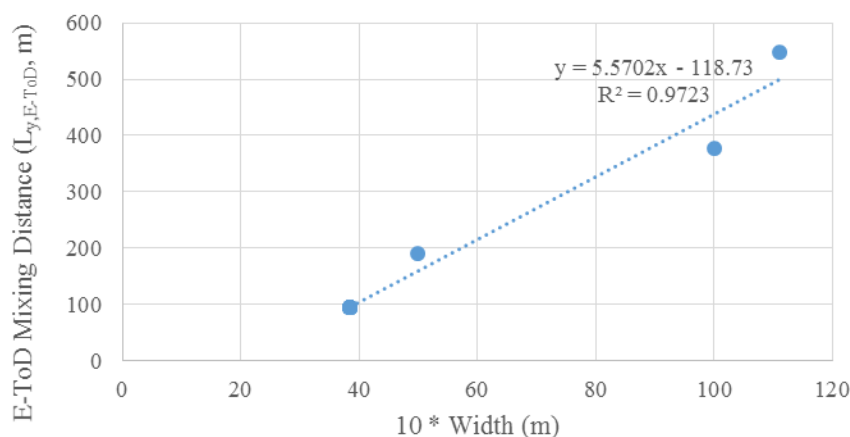


Figure 5.8. E-ToD mixing distances vs. $10 * \text{width}$ values for the 20 cases within Tersakan sub-basin

Now that all these examinations are done and some correlations are obtained, one step forward is to question whether these relationships have wider applicability or not. The results obtained in this section so far, originate from the study of the 20 particular discharge cases that are suitable for discharge limit establishment applications. These cases only include 4 out of 14 receiving water body monitoring station data within Tersakan sub-basin. Therefore, the examinations can be expanded by the incorporation of all these data. However, most of these stations do not have any suitable discharge data associated with them. To overcome this obstacle, a hypothetical discharge obtaining the following characteristics for all 14 stations is assumed for solely demonstrative purposes and all other relevant information are provided in Table 5.7:

- Contaminant of concern (CoC): Tridecane
- Environmental quality standard (EQS) = $0.05 \mu\text{g/L}$

- Discharge flowrate (Q_w) = 0.01 m³/s
- Discharge concentration (C_w) = 1 µg/L

Table 5.7. Relevant information for the expanded investigations about the relationships of mixing distances for all receiving water body stations within Tersakan sub-basin

No	ID	$L_{y,E-ToD}$ (m)	$L_{y,ASB}$ (m)	C_{DL}	C_w	$(C_{DL} / C_w)^2$	Pe	w (m)	w/d	10*w	$L_{y,E-ToD} / L_{y,ASB}$
1	20	6.05E+02	2.25E+00	1.64E+01	1.00E+00	2.69E+02	15	13.63	41	136.25	2.69E+02
2	31	3.83E+00	5.95E+00	8.03E-01	1.00E+00	6.45E-01	7	2.23	4	22.30	6.44E-01
3	32	3.83E+02	1.24E+01	5.57E+00	1.00E+00	3.10E+01	16	9.83	56	98.31	3.10E+01
4	40	3.79E+02	1.14E+01	5.77E+00	1.00E+00	3.33E+01	14	10.83	38	108.25	3.33E+01
5	97	9.47E+01	1.10E+02	9.28E-01	1.00E+00	8.61E-01	12	3.85	21	38.50	8.60E-01
6	98	1.59E+01	3.94E+03	2.88E-01	1.00E+00	8.28E-02	9	1.20	9	12.00	4.02E-03
7	109	5.47E+02	3.75E+00	1.21E+01	1.00E+00	1.46E+02	15	11.10	42	111.00	1.46E+02
8	123	2.01E+02	9.36E+00	4.63E+00	1.00E+00	2.15E+01	13	8.83	26	88.33	2.15E+01
9	125	3.76E+02	1.25E+01	5.50E+00	1.00E+00	3.02E+01	14	10.00	37	100.00	3.02E+01
10	128	1.91E+02	3.10E+02	7.86E-01	1.00E+00	6.17E-01	15	5.00	48	50.00	6.16E-01
11	991	3.23E+02	2.60E+00	1.12E+01	1.00E+00	1.24E+02	13	10.80	26	108.00	1.24E+02
12	992	3.22E+02	5.24E+00	7.83E+00	1.00E+00	6.14E+01	13	6.80	30	68.00	6.14E+01
13	993	8.17E+02	1.27E+01	8.03E+00	1.00E+00	6.45E+01	24	21.50	176	215.00	6.45E+01
14	994	1.07E+02	2.20E+03	4.99E-01	1.00E+00	2.49E-01	13	2.50	31	25.00	4.85E-02

$L_{y,ASB}$: Analytical solution based mixing distance; $L_{y,E-ToD}$: mixing distance estimated with empirical relations that are based upon a theory of dispersion; C_{DL} : discharge limit concentration of the CoC; C_w : discharge concentration of the CoC; Pe: Peclet number; w: river width; w/d: width per depth ratio

A relationship similar to the previous situation is seen in Figure 5.9. Because of the information obtained from the initial studies done with the 20 specific discharge cases, the ratio of mixing distances are plotted both against the CoC discharge concentration ratios and their squares. And, the results for the expanded examination supports the previous findings by providing perfect fitting to a 2nd degree polynomial model ($R^2 = 1$) with relatively low coefficients on the first degree and constant terms and a perfect linear correlation ($R^2 = 1$) between the mixing distance ratios and the squares of the CoC discharge concentration ratios with first degree coefficient very near to 1 and a constant value near to 0. Under these circumstances, it is safe to assume that the

previously found correlation (equation 76) holds for all stations within Tersakan sub-basin.

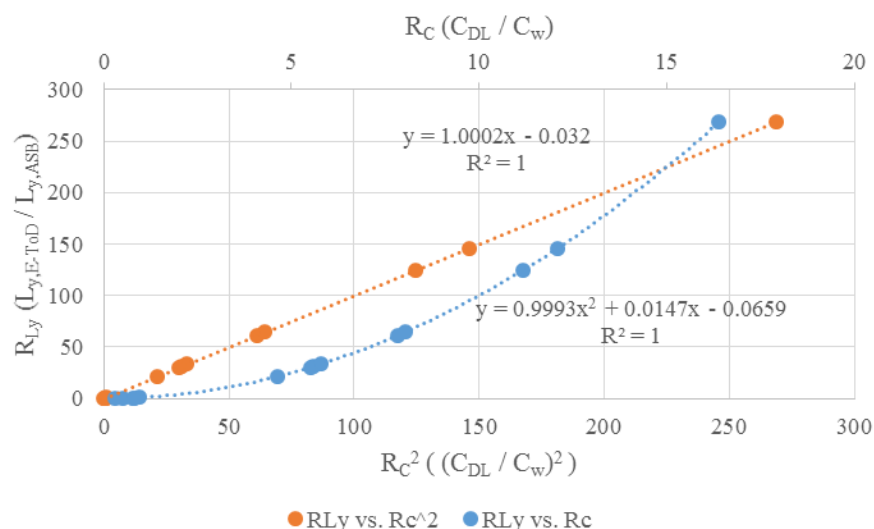


Figure 5.9. Ratio of mixing distances (R_{Ly} , E-ToD to ASB) vs. ratio of CoC discharge concentrations (R_C , discharge limit to discharge concentration) and R_C^2 in a graph with two x-axes

It should also be indicated that this generalization is only valid within Tersakan sub-basin which as previously discussed, is an area with low depth values and thus, high width to depth ratios, ranging from 4 to 176, with a mean equal to 45. Also it is a basin where the transport processes are generally dominated by advection rather than dispersion, with Pe values ranging from 7 to 24, with a mean value of 15. However, such a correlation is not counter-intuitive at all, since the ASB mixing distance dependent upon the discharge concentration of the CoC and the discharge limit of the CoC is dependent upon the discharge limit of the CoC.

The study about the relationship between E-ToD mixing distances and $10 \times$ width values can also be expanded to the 14 monitoring stations. From Figure 5.10 it can be seen that there still exists a linear relationship between the two parameters with an $R^2=0.9159$. This correlation shows that, using the “ $10 \times$ width” relation as a ballpark approximation of the mixing distance may indeed be reasonable both because of the

correlation itself and as both parameters mutually depend on receiving water body hydro-geometric and hydrodynamic parameters. However, it should not be forgotten that these findings have to be confined to Tersakan sub-basin, which is a basin with similar river characteristics throughout. For a more far-reaching generalization, these relations have to be investigated under more diverse conditions.

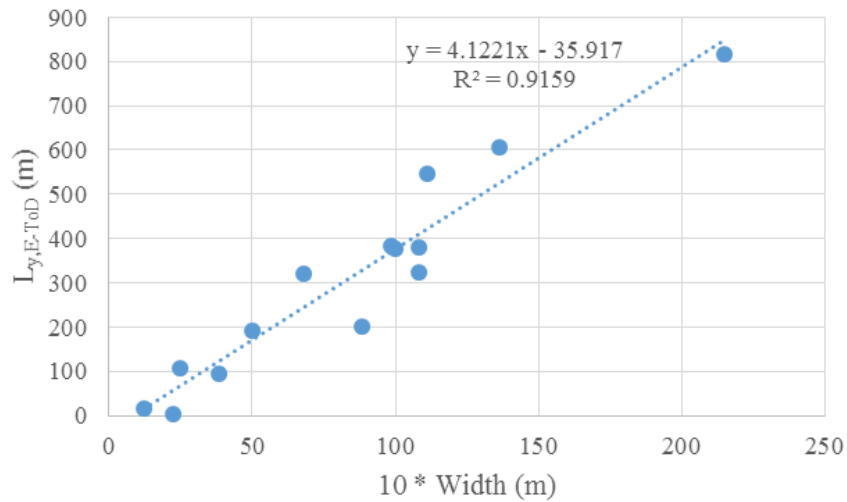


Figure 5.10. E-ToD mixing distances vs. “10 * river width” values for all the 14 receiving water body monitoring stations within Tersakan sub-basin

5.5. Relationship Between Peclet Numbers and River Width to Depth Ratios

It has been shown in the literature that the estimation efficiency of river mixing parameters can be related to receiving water body characteristic parameters such as the ratio of the river width to the depth (w/d) [46]. In particular, empirical relations that are based upon the theory of dispersion (E-ToDs) for the estimation of dispersion coefficients are reported to work better under w/d ratios greater than 10 [46]. Such dispersion coefficients are utilized (see equations 18, 26 and 32) as part of the approach developed for the establishment of discharge limits in the study. So, w/d ratio becomes an important parameter to follow for this study.

On the other hand, Peclet number (Pe), as a dimensionless number that provides information about the dominant mass transport processes in a system, is a major deciding factor that aids determining the analytical solution that will be utilized in the discharge limit establishment approach developed in this study, Therefore Pe is also quite significant for the study.

Pe when compared to w/d ratio is a more complex parameter. It depends on other parameters that have to be approximated such as L_y (transverse characteristic mixing distance, see equation 35) and D_x (longitudinal dispersion coefficient, see equation 32), as well as fundamental parameters such as river velocity, whereas w/d ratio is only dependent upon two simple receiving water body hydro-geometric parameters, river width and depth.

Under such circumstances, it would be useful if the more complex Pe could be approximated from w/d ratio which is a simple yet important receiving water body characteristic parameter.

To investigate whether any correlation exists between Pe and w/d ratio, data collected from Tersakan sub-basin is used and first data related to the 20 discharge cases suitable for use in the discharge limit estimation approach developed in the study are examined.

According to this examination, Pe and w/d ratio data is able to be fitted either to a linear, an exponential, a logarithmic, a polynomial or a power function with high R^2 values (All ≥ 0.99 , the highest being the power function fit, with $R^2 = 0.9991$, see Figure 5.11).

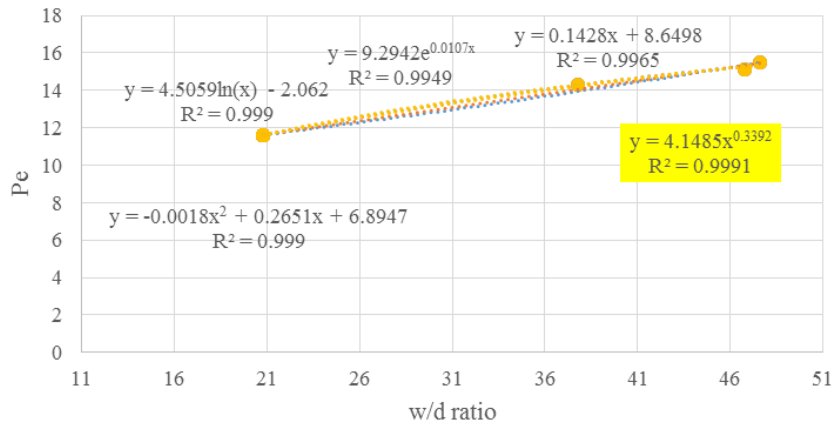


Figure 5.11. Pe vs. w/d ratio graph with relevant equations and R^2 values for various fits for the 20 discharge cases within Tersakan sub-basin that are suitable for discharge limit estimation applications

Building on these results, the investigation is then, expanded to cover all 14 receiving water body monitoring stations within Tersakan sub-basin (see Table 3.5 and Table 3.8). This time, best possible options are narrowed down to logarithmic, 2nd and 3rd order polynomial and power function fits with the highest R^2 (=0.9995) value from the power function fit (refer to Figure 5.12).

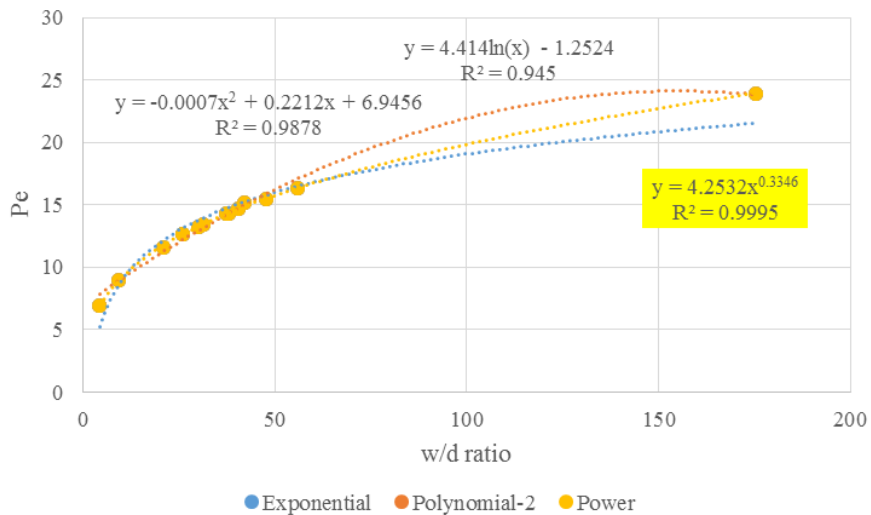


Figure 5.12. Pe vs. w/d ratio graph with relevant equations and R^2 values for various fits for all 14 receiving water body monitoring stations within Tersakan sub-basin

To sum this section up, for the receiving body monitoring station points within Tersakan sub-basin, there seems to be a correlation between w/d ratio and Pe values that can be best mathematically expressed through a power function. It can be argued that with the use of such a relation, Pe values for other points on Tersakan sub-basin could be approximated with only river width and depth values available.

5.6. Advantages and Limitations of the Discharge Limit Establishment Approach

The EQS-based discharge limit establishment approach in itself has some limitations, since not all conditions of discharge can realistically be modeled through simple analytical solutions of the advective-dispersive mass transport equation. All cases that would need the use of more advanced modeling tools that employ numerical techniques such as CORMIX are listed below and also can be seen from Table 4.1 and Figure 4.3:

1. Intermittent (not continuous) discharge
2. Unsteady, continuous discharge with either advection negligible with respect to dispersion ($Pe \ll 1$) or vice versa ($Pe \gg 1$)
3. Unsteady, continuous discharge with both considerable advection, dispersion ($0.1 < Pe < 10$), and vertical and/or transverse dispersion
4. Steady-state, continuous discharge with both advection (with respect to dispersion, $Pe \ll 1$), and biodegradation (with respect to transport, $Da \ll 1$) negligible and considerable vertical and/or transverse dispersion
5. Steady-state, continuous discharge with negligible advection (with respect to dispersion, $Pe \ll 1$), considerable biodegradation (with respect to transport, $Da \ll 1$), and vertical and/or transverse dispersion

In such cases, to run more complex models extensive amount of data would be required, and therefore the approach developed in this text does not actually aim to be a substitute to be used under these highly complex conditions. Its objective is to offer an approach that is both based on solid theoretical knowledge and also can be applied

with minimum amount of data to maximum number of conditions. Having clear assumptions and limitations and not claiming to be a universal tool can also be interpreted as a strength of the approach. Thus, it also acts a screening tool, directing the user in cases where more advanced models are needed for discharge limit establishment.

5.7. Applicability in Turkey

As indicated in the section regarding water quality monitoring (WQM) of Chapter 2: Literature Survey, implementation of systematic, frequent and extensive WQM programs at the level of each water basin is crucial for the identification of receiving water body characteristics, which form the basis of the estimation of mixing parameters and therefore the approximation of mixing zones and EQS-based discharge limits. Hence, although the developed discharge limit establishment tool has lower data requirements compared to its counterparts, its applicability directly depends on the availability of receiving water body quality data.

Turkey, which is where this study takes place, despite having a rather long history of WQM experiences beginning from the late 1970s, and having gone through a rapid network development during the first 20 years of this experience [16], now faces serious challenges.

Due to the requirements of more recent environmental legislations (such as the Surface Water Quality Regulation promulgated in 2012 as part of Ministry of Agriculture and Forestry's efforts for harmonizing with the European Commission's Directive 2000/60/EC, or the Water Framework Directive [13], [28]), WQM has to become much more systematic and current legislative objectives should primarily determine the locations of monitoring stations, monitoring frequencies and water quality parameters monitored [50].

Nevertheless, in the last two decades national efforts of WQM has become much more dispersed. In 1999, only two governmental agencies were involved in WQM [16], yet as of 2014 this number has increased to more than nine [50]. All of these separate

agencies, ranging from general directorates of various ministries to municipalities, have different legislative or administrative objectives for their own WQM efforts [50]. The formation of a systematic, frequent and extensive nationwide WQM program to produce the necessary information that is needed for the protection of national waters requires a considerable amount of financial and human resources. To achieve this, all these dissipated efforts has to urgently be harmonized with legislative environmental protection goals and thus be consolidated.

The current condition of WQM in Turkey is clearly unfeasible for the applicability of the EQS-based discharge limit establishment developed as part of the study. One quite evident indicator of this is the fact that the data for the case study site could not be obtained from governmental agencies and rather had to be collected for a limited number of seasons as part of a project by a group of researchers from Munzur University (Tunceli, Turkey).

CHAPTER 6

SUMMARY, CONCLUSIONS & RECOMMENDATIONS

In this final chapter, the objectives and findings of the thesis is summarized and concrete conclusions are derived. Some suggestions for further studies are also mentioned.

6.1. Summary and Conclusions

Control of point source pollution due to discharges to rivers is a crucial part of the urgent measures that needs to be taken care of that is caused by increased human population and activity since it may result in serious adverse impacts on both human health and the well-being of the ecosystem as a whole.

Many countries that at different stages of their development are now aware of this, and environmental legislations around the world have started to cover the topic of limiting the discharges of potentially harmful substances to river systems. The first and most fundamental level of these limits is the prevention or reduction of the discharge of any contaminant of concern (CoC) into rivers to the highest degree that is both technically and economically achievable. If the employment of such techniques are not sufficient to maintain the receiving water body at an acceptable quality, then more stringent limits become part of the discussion. These more stringent limits or environmental quality standards (EQS) based discharge limits, cannot easily be determined. Usually the process of EQS-based discharge limit establishment requires considerable amount of data that is sufficient to characterize both conditions of the discharge and the receiving water body.

The attempt and aim of this study is to develop a new approach for the establishment of EQS-based discharge limits, one that can be used under many cases without the need of extensive data. To achieve this, it demands only the fundamental parameters

of river characteristics, which are depth, width, slope, velocity, and flowrate. And for the discharge, the concentration of the CoC and the flowrate alone are sufficient. The discharge limit establishment tool, then uses these data to estimate river mixing parameters according to best available empirical relations and select among a menu of 11 different analytical solutions of the generic advective-dispersive mass transport equation, the most suitable one for the specific case. If none of these solutions fit the particular case, then this would indicate that more advanced modeling is inevitable for the case.

The advantage of such an approach is that it suggests an initial screening, so that one can confidently know whether the utilization of this tool or approach is sufficient or if the discharge conditions oblige the implementation of more complex mixing models. Therefore, its strength results from its clearly stated limitations. Another advantage of it is that, it is open for development. Considering the rapid technological advancements in this era, it is safe to assume that progress will be seen in the area of river mixing as well. Any such progress can easily be implemented to the approach in the future. Using a commonly-known and easy-to-learn programming environment such as MATLAB favors this as well.

The applicability of this new approach has been tested with a case study on Tersakan sub-basin of Yeşilırmak water basin, which is identified as particularly polluted due to intense agricultural and industrial activities.

Before all, the hydro-geometric and hydrodynamic characteristics of Tersakan sub-basin is examined. All parameters including width, depth, mean velocity, flowrate, characteristic mixing distances and dispersion coefficients, except Peclet numbers and width per depth ratios, fluctuate non-negligably between low and high flowrate seasons. Therefore, it should be indicated for Tersakan sub-basin that discharge limits can also fluctuate significantly throughout seasons and discharge limits estimated with all-time average parameters may create EQS violations during low flowrate seasons especially if discharge CoC mass loading is greater than or equal to 60-70% of the

discharge limit. Fortunately for our case study, receiving body monitoring data is collected predominantly during low flowrate seasons for the cases that are suitable for discharge limit estimation applications.

One important observation about the hydro-geometric characteristics of the receiving body stations that are associated with the discharge cases that are suitable for discharge limit establishment within Tersakan sub-basin is that the transverse dimension (river width) is more than one order of magnitude greater than the vertical dimension (river depth). There is more than two orders of magnitude difference between transverse and vertical characteristic mixing distances as well (former one being greater than the latter). Hence, for the discharge limit estimation studies in Tersakan sub-basin, all cases are assumed have 2-D mixing (concentration differences in the vertical direction are neglected).

Nevertheless, for the discharges within Tersakan sub-basin that are suitable for the application of the EQS-based discharge limit establishment approach, the results show that, although some of them necessitate more caution for the future, none of these discharges require immediate preventive action for the reduction of the relevant mixing zones, i.e. all seem permissible. Yet, all of these permissible discharges are also categorized according to their future risk potentials by considering the amount of discharge limit consumed by the actual discharge. In regard to this categorization, 3 discharges (%15) seem to possess very high future risk ($\geq 50\%$ of discharge limit allocated already; Merzifon OIZ-Tridecane, Merzifon OIZ-Ni, Amasya Sugar Factory-Bis(2-ethylhexyl) terephthalate) and 3 of them (%15) appear to have high future risk (between 10-50% of discharge limit allocated already; Merzifon OIZ-NH₄-N, Merzifon OIZ-TP, and Merzifon OIZ-Free CN). The remaining 70% is of moderate, low or very low future risk groups.

Aside from this, two of these 20 discharges (NH₄-N and TP of Merzifon OSB discharge station) that are permissible with respect to their effect on downstream river

quality, seem not to comply with the best available techniques associated discharge limits that are set in the Turkish Water Pollution Prevention Regulation.

This case study can only be regarded as partially successful, because of the fewness of the number of data suitable for discharge limit estimation. Thus, all options of the solutions menu could not be applied. One reason of this is the fact that Tersakan sub basin actually does not have good chemical water statues at all points. Discharge limits could not be established for many discharged CoCs because the upstream receiving water body concentration were above the permissible EQS level.

Beside discharge limits, mixing distances are also estimated both by empirical relations that are based on a theory of dispersion (E-ToD) and by analytical solutions (ASB). The E-ToD mixing distance is used in the estimation of discharge limits. On the other hand, the ASB mixing distances are based upon the discharge concentrations of the CoC and therefore cannot generate discharge limits. However, if a discharge is permissible by the E-ToD mixing distance based discharge limit, then the ASB mixing distance can be used to reduce the size of the mixing zone and allow for a second discharge the of the same CoC at a point nearer to the initial point of discharge, rendering the permission conditions less strict by widening the area where a CoC could be discharged to the receiving water body.

Some correlations, that can only be justified for Tersakan sub-basin between various receiving water body characteristic parameters are also found. One of these is the linear relationship between E-ToD mixing distances with the ballpark values obtained by the very simple mixing distance approximation method suggested by the EU [32], which is “ $10 \times \text{river width}$ ”. This suggests that this approximation although being rough, may not be unreasonable or arbitrary. Another correlation also seems to exist between Peclet numbers and width per depth ratios, which are both characteristic parameters that are indicative of the conditions prevailing at the receiving water body. Such an interrelation implies that Pe 's which are much more detidious to estimate could be approximated from the w/d ratios. To strengthen all such correlations and claims, these

investigations have to be extended to a higher number of more diverse river conditions.

Similar to any approach that includes mathematical modeling, the accuracy of the model inputs, or the receiving water body and discharge monitoring data for this particular case, directly affect the accuracy of the modeling results. Therefore, unless there exists a sound water quality monitoring (WQM) program, the best tools for mixing zone estimation or discharge limit establishment would not produce realistic results. Implementation of systematic and widespread WQM programs continues to be a challenge in many parts of the world including Turkey. To make more use of the approach developed in the text, the obstacles in this area have to at least be partially overcome.

Also, to further increase the utility and applicability of the developed approach, it can both be adapted to a web interface and be coupled with an online database that would hold all relevant monitoring data. Thus, the online system could operate automatically to reassess mixing zones and discharge limits as new data enters the database inform all the stakeholders about the current situation.

To sum up this study has provided important information regarding point source pollution within the study site, Tersakan sub basin of Yeşilırmak river. This initial step of the identification of discharge limits for different points on Tersakan Creek, can also help shaping the future industrial development in the region, by providing a perspective on current pollutant loads and the dilution capacity of the receiving water body.

Finally, the study has successfully introduced an integrated and novel approach for the approximation of mixing zone and the estimation of discharge limits. The approach has clear and definite limitations and therefore it serves as a screening tool as well, which could direct the user to proceed with more advanced techniques if receiving water body and/or discharge conditions necessitate it. It does not suggest to be a one-size-fits all, universal solution for all cases. It has realistic objectives and claims. It is also able to

coherently combine many parts of what has been discovered in the field of river mixing. To do so, it follows a modular approach so that future scientific developments can easily be implemented to it. Hence, the novel approach developed throughout this study has many aspects to it to become of much greater service in the near future as well.

6.2. Recommendations for Further Studies

The approach developed in the study for the establishment of discharge limits for point source discharges to rivers, is one that is open to further improvement since it is based on empirical relations and analytical solutions that are compiled from the literature [31], [38], [49], [39]–[43], [45], [46], [48]. River mixing is still not fully understood and research in this area continues at an appreciable rate. This indicates that in time, better empirical relations for the mixing parameters or more accurate theories of mixing or semi-analytical solutions for more diverse conditions will most probably be developed. And the tool developed in this study can be further advanced by the adoption of relevant state-of-the-art techniques.

Additionally, the correlations found (between the mixing distances that are estimated via empirical relations that are based upon a theory of dispersion (E-ToD mixing distances) and “ $10 * \text{width}$ ”; or between Peclet numbers and width per depth ratios) and the claims suggested related to those correlations have to be corroborated by expanding the investigation to include an increased number of points representing a wider range of diverse river conditions than what can be found within Tersakan sub-basin.

Another important point is about increasing the widespread applicability of the approach. This approach, far from being just for the mere satisfaction of academic interest, can easily be used as a decision support mechanism for governmental agencies for discharge permitting procedures. The main obstacle with the current version before this is that its computer program is written in MATLAB, which is a commercial software and although having an easily learnable language and user interface, it still is not suitable for the basic user. However, with the aid of a web

specialist, it can easily be adapted to a web interface that can easily be populated with data either manually or automatically. This hypothetical web interface can also be connected to an online database that holds all relevant monitoring data about receiving water bodies and discharges, and can be programmed to be rerun according to monitoring frequencies and thus, instantly have updated permissible discharge concentration or load information for all discharges of all kinds of contaminants.

REFERENCES

- [1] M. K. Jermar, *Water Resources and Water Management*. Amsterdam, the Netherlands: Elsevier, 1987.
- [2] R. Pearson, “Environmental Indicators of Healthy Water Resources,” in *Water Resources: Health, Environment and Development*, B. H. Kay, Ed. New York, NY: E & FN Spon, 1999.
- [3] T. H. Y. Tebbutt, *Water Quality Control*, 5th ed. Oxford: Butterworth-Heinemann, 1998.
- [4] Z.-G. Ji, *Hydrodynamics and Water Quality: Modeling Rivers, Lakes and Estuaries*. John Wiley & Sons, 2008.
- [5] M. I. Lvovitch, “World water balance (general report),” *Symp. World Water Balanc.*, no. 93, pp. 401–415, 1971.
- [6] H. F. Hemond and E. J. Fechner, “Surface Waters,” in *Chemical Fate and Transport in the Environment*, 3rd ed., Waltham, MA: Elsevier, 2015, pp. 75–218.
- [7] C. Pradinaud *et al.*, “Defining freshwater as a natural resource: a framework linking water use to the area of protection natural resources,” *Int. J. Life Cycle Assess.*, vol. 24, no. 5, pp. 960–974, 2019.
- [8] T. Sonderegger *et al.*, “Towards harmonizing natural resources as an area of protection in life cycle impact assessment,” *Int. J. Life Cycle Assess.*, vol. 22, no. 12, pp. 1912–1927, 2017.
- [9] J. Dewulf *et al.*, “Rethinking the area of protection ‘natural resources’ in life cycle assessment,” *Environ. Sci. Technol.*, vol. 49, no. 9, pp. 5310–5317, 2015.
- [10] E. R. Alley, *Water Quality Control Handbook*, 2nd ed., vol. 24. New York, NY: McGraw-Hill, 2007.
- [11] US EPA, “Introduction to the Clean Water Act,” 2011.
- [12] European Comission, *COUNCIL DIRECTIVE 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control*. 1996, p. L257/26-40.
- [13] European Comission, *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*. 2000, p. L327/1-72.
- [14] European Comission, *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,. 2008, p. L348/84-97.
- [15] UNEP and WHO, *Water Quality Monitoring: A practical guide to the design and implementation of freshwater quality studies and monitoring programmes*, 1st ed. London, UK: E & FN Spon, 1996.
 - [16] N. B. Harmancioglu, O. Fistikoglu, S. D. Ozkul, V. P. Singh, and M. N. Alpaslan, *Water Quality Monitoring Network Design*, 1st ed. Dordrecht: Springer-Science+Business Media, B. V., 1999.
 - [17] R. O. Strobl and P. D. Robillard, "Network design for water quality monitoring of surface freshwaters: A review," *J. Environ. Manage.*, vol. 87, no. 4, pp. 639–648, 2008.
 - [18] T. H. Nguyen, B. Helm, H. Hettiarachchi, S. Caucci, and P. Krebs, "The selection of design methods for river water quality monitoring networks: a review," *Environ. Earth Sci.*, vol. 78, no. 3, pp. 1–17, 2019.
 - [19] S. Behmel, M. Damour, R. Ludwig, and M. J. Rodriguez, "Water quality monitoring strategies — A review and future perspectives," *Sci. Total Environ.*, vol. 571, pp. 1312–1329, 2016.
 - [20] CIS WFD, *Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Guidance document - No. 7 Monitoring under the Water Framework Directive*. Luxembourg, 2003.
 - [21] R. G. Quimpo and J. Yang, "Sampling Considerations in Stream Discharge and Temperature Measurements," *Water Resour. Res.*, vol. 6, no. 6, pp. 1771–1774, 1970.
 - [22] US EPA, "NPDES Permit Writers' Manual," ity Press, 2010.
 - [23] European Comission, *DIRECTIVE 2008/1/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 15 January 2008 concerning integrated pollution prevention and control (Codified version)*, vol. L24. 2008, pp. 8–29.
 - [24] European Comission, *DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast)*, vol. L334. 2010, pp. 17–119.
 - [25] European Comission, "The Industrial Emissions Directive," 2019. [Online]. Available: <https://ec.europa.eu/environment/industry/stationary/ied/legislation.htm>. [Accessed: 10-Aug-2019].

- [26] European Commission, “Reference documents under the IPPC Directive and the IED,” 2019. [Online]. Available: <https://eippcb.jrc.ec.europa.eu/reference/>. [Accessed: 10-Aug-2019].
- [27] Republic of Turkey Official Gazette, *Water Pollution Control Regulation [in Turkish]*. 2004.
- [28] Republic of Turkey Official Gazette, *Surface Water Quality Regulation [in Turkish]*. 2012.
- [29] US EPA, “Technical support document for water quality-based toxic control,” 1991.
- [30] N. Babbedge *et al.*, “Technical Guidelines for the Identification of Mixing Zones,” 2010.
- [31] H. B. Fischer, E. J. List, R. C. Y. Koh, J. Imberger, and N. H. Brooks, “Mixing in Inland and Coastal Waters,” *Mix. Inl. Coast. Waters*, pp. 1–483, 1979.
- [32] European Communities, “Technical Background Document on Identification of Mixing Zones,” no. December. p. 34, 2010.
- [33] D. R. Maidment and D. Tarboton, “Computation of Slope,” 2011.
- [34] Purdue University Dept. of Chemistry, “Half Lives,” 2019. [Online]. Available: <https://www.chem.purdue.edu/gchelp/howtosolveit/Kinetics/Halflife.html>.
- [35] TOXNET, “Hazardous Substance Data Bank (HSDB),” 2019. [Online]. Available: <https://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>.
- [36] FAO, “Fenpropimorph,” in *Joint FAO/WHO Meeting on Pesticide Residues (JMPR) Evaluation 1995*, 1995.
- [37] J. D. Wolt, “Environmental Fate of Ethalfluralin,” 1997, pp. 65–90.
- [38] S. A. Socolofsky and G. H. Jirka, “Special topics in mixing and transport processes in the environment,” *Coast. Ocean Eng. Div.*, no. 5th Edition, 2005.
- [39] H. Sharma and Z. Ahmad, “Transverse mixing of pollutants in streams: a review,” *Can. J. Civ. Eng.*, vol. 41, no. 5, pp. 472–482, 2014.
- [40] N. Elhadi, A. Harrington, I. Hill, Y. L. Lau, and B. G. Krishnappan, “River mixing - A state-of-the-art report,” *Can. J. Civ. Eng.*, vol. 11, pp. 585–609, 1984.
- [41] J. C. Rutherford, *Handbook on Mixing in Rivers*, vol. 26, no. 26. 1981.
- [42] K. O. Baek and I. W. Seo, “On the methods for determining the transverse dispersion coefficient in river mixing,” *Adv. Water Resour.*, vol. 90, pp. 1–9, 2016.

- [43] S. C. Chapra, *Surface Water-Quality Modeling*. New York, NY: McGraw-Hill, 1997.
- [44] H. B. Fischer, “The Effect of Bends on Dispersion in Streams,” *Water Resour. Res.*, vol. 5, no. 2, pp. 496–506, 1969.
- [45] K. O. Baek and I. W. Seo, “Estimation of the transverse dispersion coefficient for two-dimensional models of mixing in natural streams,” *J. Hydro-Environment Res.*, vol. 15, pp. 67–74, 2017.
- [46] Z.-Q. Deng, V. P. Singh, and L. Bengtsson, “Longitudinal Dispersion Coefficient in Straight Rivers,” *J. Hydraul. Eng.*, vol. 127, no. 11, pp. 919–927, 2001.
- [47] OECD, “Guiding Principles of Effective Environmental Permitting Systems,” Paris, France, 2007.
- [48] A. Fedi, M. Massabò, O. Paladino, and R. Cianci, “A new analytical solution for the 2D advection-dispersion equation in semi-infinite and laterally bounded domain,” *Appl. Math. Sci.*, vol. 4, no. 75, pp. 3733–3747, 2010.
- [49] M. Massabó, R. Cianci, and O. Paladino, “An analytical solution of the advection dispersion equation in a bounded domain and its application to laboratory experiments,” *J. Appl. Math.*, vol. 2011, 2011.
- [50] C. Gök, “The Chemical Monitoring and the Determination of Monitoring Points for Surface Waters in Turkey as A European Union Candidate [in Turkish],” Republic of Turkey Ministry of Agriculture and Forestry, 2014.

APPENDICES

A. MATLAB CODES FOR THE DISCHARGE LIMIT ESTABLISHMENT APPROACH

In this section, MATLAB codes for the estimation of discharge limits are given.

dislim.m (Estimates discharge limits for equations 43 and 47)

```
clear all; close all; clc;

load <relevant_data>;

% kg/d or tonne/d
% if Cw and EQS given in microgram/L == kg/d
% if Cw and EQS given in mg/L == tonne/d

Cf_lim=[ eqs.*4*pi()*Ly.*sqrt(Dy.*Dz)./Qw ...
%dis lim microg/L or mg/L (3-D)
        eqs.*v.*d.*sqrt(4*pi()*Dy.*Ly./v)./Qw ...   %(2-D)
        eqs.*4*pi()*Ly.*sqrt(Dy.*Dz)/1000/1000*3600*24
... %dis lim kg/d or ton/d (3-d)
eqs.*v.*d.*sqrt(4*pi()*Dy.*Ly./v)/1000/1000*3600*24
...   %(2-D)];
```

md_asb_2d.m (Function for the estimation of the 2-D ASB mixing zone)

```
function [ err ] = md_asb_2d( l1,mm )

% For the following conditions:
%
% - Steady-state & continuous discharge
% - Pe >> 1
% - Negligible decay
% - 2-D mixing (complete mixing
%   in the vertical direction
%   at the point of discharge)
% - Analytical-solution-based
%   mixing distances are used

format short e

load <relevant_data>;

m=21; % number of intervals

Cw=Cw0 (mm); % discharge concentration

y=linspace(0,w(mm),m);
z=linspace(0,d(mm),m);

nm=2; % number of imaginary sources

n1=-nm:nm; % imaginary source counter

x=linspace(0,l1,2*m);

C=zeros(2*m,m,m); %initialization

sum=zeros(2*m,m,m); %initialization
```

md_asb_2d.m (cont'd)

```

        for i=2:length(x)
            for j=1:length(y)
                for k=1:length(z)
                    for p=1: numel(n1)
                        sum(i,j,k)=sum(i,j,k)+exp(-
v(mm)*( (y(j)-2*n1(p)*w(mm))^2)/(4*Dy(mm)*x(i)));
                    end

C(i,j,k)=Cw*Qw(mm)/(v(mm)*d(mm)*sqrt(4*pi*Dy(mm)*x(i)/
v(mm)))*sum(i,j,k);
                end
            end
        end

assignin('base','C',C);

err=((C(2*m,1,1)-eqs(mm))/eqs(mm))^2;

assignin('base','sum',sum(:));

assignin('base','err',err);

assignin('base','x',x);
assignin('base','y',y);
assignin('base','z',z);

end

```

md_asb_3d.m (Function for the estimation of the 3-D ASB mixing zone)

```
function [ err ] = md_asb_3d( l1,mm )

% For the following conditions:
%
% - Steady-state & continuous discharge
% - Pe >> 1
% - Negligible decay
% - 3-D mixing
% - Analytical-solution-based
%   mixing distances are used

format short e

load <relevant_data>;

m=21; % number of intervals

Cw=Cw0 (mm); % discharge concentration

y=linspace(0,w (mm) ,m) ;
z=linspace(0,d (mm) ,m) ;

nm=12; % number of imaginary sources

% imaginary source counters

n1=-nm:nm;
n2=n1;
n2 (n2==0)=[ ];

    x=linspace(0,l1,2*m) ;

        C=zeros (2*m,m,m) ; %initialization

        sum1=zeros (2*m,m,m) ; %initialization
        sum2=zeros (2*m,m,m) ; %initialization
```

md_asb_3d.m (cont'd)

```

        for i=2:numel(x)
            for j=1:numel(y)
                for k=1:numel(z)
                    for p=1:numel(n1)
                        sum1(i,j,k)=sum1(i,j,k)+exp(-
v(mm)*(y(j)-2*n1(p)*w(mm))^2)/...
                        (4*Dy(mm)*x(i))-
v(mm)*(z(k)^2)/(4*Dz(mm)*x(i)));
                    end
                    for r=1:numel(n2)
                        sum2(i,j,k)=sum2(i,j,k)+exp(-
v(mm)*(z(k)-2*n2(r)*d(mm))^2)/...
                        (4*Dz(mm)*x(i))-
v(mm)*(y(j)^2)/(4*Dy(mm)*x(i)));
                    end
                end
            end
        end

C(i,j,k)=Cw*Qw(mm)/(4*pi*x(i)*sqrt(Dy(mm)*Dz(mm)))*(su
m1(i,j,k)+sum2(i,j,k));
    end
end

assignin('base','C',C);

err=((C((2*m-1),1,1)-eqs(mm))/eqs(mm))^2;

assignin('base','sum1',sum1);
assignin('base','sum2',sum2);
assignin('base','sum_all',sum1(:)+sum2(:));

assignin('base','err',err);

assignin('base','x',x);
assignin('base','y',y);
assignin('base','z',z);

end

```

md_asb_exe.m (Runs any ASB mixing zone estimation function)

```
clear all; close all; clc

load <relevant_data>;

for mm=1:length(w)
    err2=<md_asb_#>(50,mm); % # can be 2d, 3d or else
    C2=C;
    x2=x;
    solite=sprintf('\n[ASB]'); % for the plot title
    solna=sprintf('_asb'); % for the image name
    plots_lon_tra; % script that draws longitudinal
    and transverse concentration profiles
end
```

plots_lon_tra.m (Draws longitudinal and transverse concentration profiles, given that C is estimated beforehand)

```
x2(1)=[]; % exclude x=0 since it produces C=NaN

C2(1, :, :)=[]; % exclude x=0 since it produces C=NaN
C2=reshape(C2,length(x2),length(y),length(z));

% X vs C Graph

XGraph=figure;

lontit=sprintf('Concentration vs. Longitudinal
distance (Tersakan Discharge #0.2d)',mm); % plot
title

C2x=reshape(C2(:, :, 1),length(x2),length(y)); %
concentration values at z = 0 m
eqsx=ones(length(x),1); % initialization for eqs line
eqsx=eqsx*eqs(mm); % eqs line

plot(x2,C2x(:,1),'-o',x2,C2x(:,ceil(length(y)/2)),'-
*',x2,C2x(:,length(y)),'-^',x,eqsx,'m'); % draw
profiles @y=0, @y=mid-point; @y=end-point
xlabel('Longitudinal distance (m)');
ylabel('CoC(mm)');
```

plots_lon_tra.m (cont'd)

```
ylim([0 max([0.06,max(max(C2x))])]);
tratit=sprintf('Concentration vs. Transverse distance
(Tersakan Discharge #%0.2d)',mm);

C2y=reshape(C2(:, :, 1),length(x2),length(y));

legend(sprintf('@y=%0.2fm',y(1)),sprintf('@y=%0.2fm',y
(ceil(length(y)/2))),sprintf('@y=%0.2fm',y(end)), 'EQS'
)

legend(sprintf('@y=%0.2fm',y(1)),sprintf('@y=%0.2fm',y
(ceil(length(y)/2))),sprintf('@y=%0.2fm',y(end)), 'EQS'
) % name profiles @y=0, @y=mid-point; @y=end-point
hold off;
title([lontit,solite]); % write plot title

% settings to save image file
set(XGraph,'paperunits','centimeters')
set(XGraph,'paperposition',[0 0 15 10]);

imanalon=sprintf('XvsC%d',mm);
imanalon=[imanalon,solna];
print(XGraph,imanalon,'-dpng','-r150')

% Y vs C Graph

YGraph=figure;

tratit=sprintf('Concentration vs. Transverse distance
(Tersakan Discharge #%0.2d)',mm); % plot title

C2y=reshape(C2(:, :, 1),length(x2),length(y)); %
concentration values at z = 0 m

eqsy=ones(length(y),1); % initialization for eqs line
eqsy=eqsy*eqs(mm); % eqs line

plot(y,C2y(1,:), '-o',y,C2y(ceil(length(x2)/2),:),'-
*',y,C2y(length(x2),:),'-^',y,eqsy,'m'); % draw
profiles @x=x(1), @x=mid-point; @x=end-point

xlabel('Transverse distance (m)');
```

plots_lon_tra.m (cont'd)

```
xlabel('Transverse distance (m)');
ylabel(CoC(mm));
ylim([0 max([0.06,max(max(C2y))])]);
legend(sprintf('@x=%0.2fm',x2(1)),sprintf('@x=%0.2fm',
x2(ceil(length(x2)/2))),sprintf('@x=%0.2fm',x2(end)), '
EQS') % write profiles @x=x(1), @x=mid-point; @x=end-
point
hold off;
title([tratit,solite]); % write plot title

% settings to save image file

set(YGraph,'paperunits','centimeters')
set(YGraph,'paperposition',[0 0 15 10]);

imanatra=sprintf('YvsC%d',mm);
imanatra=[imanatra,solna];
print(YGraph,imanatra,'-dpng','-r150')
```

dle_excel.m (Creates an Excel workbook where worksheets contain x-sectional concentration distributions for all y and z values, given that C is estimated beforehand)

```
% initialization for column and row heading
xax=num2cell(zeros(length(x),1));
yax=num2cell(zeros(length(y),1));
zax=num2cell(zeros(length(z),1));
% arrays of column and row heading
for k=1:length(x)
    xax(k)=cellstr(sprintf('x=%0.2fm',x(k)));
end

for k=1:length(y)
    yax(k)=cellstr(sprintf('y=%0.2fm',y(k)));
end

for k=1:length(z)
    zax(k)=cellstr(sprintf('z=%0.2fm',z(k)));
end
```

dle_excel.m (cont'd)

```
xax=xax';
xax=cellstr(xax);
yax=cellstr(yax);
zax=cellstr(zax);

% prompt for the name of the Excel file
xlsname=input('Input a name for the Excel
file\n(without any extensions):\n','s');
xlsname=sprintf(xlsname, '.xls');

% write worksheets for each z value
for k=1:11
    C1=C(:, :, k);
    C1=C1';
    C1=num2cell(C1);
    C1=[xax;C1];
    C1=[blanks(1);yax] C1;
    namez=sprintf('z%0.2fm',z(k));
    xlswrite(xlsname, C1, namez);
end

% write worksheets for each y value
for k=1:11
    C2=(reshape(C(:, k, :), [numel(x) numel(z)]));
    C2=C2';
    C2=num2cell(C2);
    C2=[xax;C2];
    C2=[blanks(1);zax] C2;
    namey=sprintf('y%0.2fm',y(k));
    xlswrite(xlsname, C2, namey);
end
```

dle_ani.m (Creates MPEG-4 video files that show the progression of the mixing zones, given that C is estimated beforehand)

```
% initialization for 3-d surface plot (x,y,C) or
(x,z,C)
[x_xy,y_xy]=meshgrid(x,y);
[x_xz,z_xz]=meshgrid(x,z);
% initialization for 3-d eqs surface
eqs_xy=ones(size(x_xy))*eqs(mm);
eqs_xz=ones(size(x_xz))*eqs(mm);

C_tra=C(:,:,1)'; % transverse conc. distributions
C_ver=(reshape(C(:,1,:),[numel(x) numel(z)]))'; %
verticle conc. distributions

k_t=1; % initialization for video frame counter

dle_fig=figure;
set(gcf,'Renderer','ZBuffer')

for e=2:length(C)
    % transverse conc. distribution surface plot loop
    subplot(2,1,1)

    set(dle_fig,'unit','Normalized','OuterPosition',[0 0 1
    1]);

    surf(x_xy(:,1:e),y_xy(:,1:e),C_tra(:,1:e),'edgecolor',
    'none');
    shading 'interp';
    xlabel('Longitudinal distance (m)');
    ylabel(sprintf('Transverse distance (m)\nw = %0.2f
    m',w(mm)));
    hold on;
    surf(x_xy,y_xy,eqs_xy,'FaceColor',[0.5,0,0.5],'edgecol
    or','none');
    hold off;
    cb=colorbar;
    ylabel(cb,CoC(mm));
    view(0,90);
```

dle_ani.m

```
% vertical conc. distribution surface plot loop
subplot(2,1,2)

surf(x_xz(:,1:e),z_xz(:,1:e),C_ver(:,1:e),'edgecolor',
'none');
shading interp;
xlabel('Longitudinal distance (m)');
ylabel(sprintf('Vertical distance (m)\nd = %0.2f
m',d(mm)));
set(gca,'Ydir','reverse');
hold on;
surf(x_xz,z_xz,eqs_xz,'FaceColor',[0.5,0,0.5],'edgecol
or','none');
hold off;
cb=colorbar;
ylabel(cb,CoC(mm));
view(0,90);

F(k_t)=getframe(dle_fig);
k_t=k_t+1;
end

hold off;
% video writer
video=VideoWriter(sprintf('dle_ani_%0.2d.mp4',mm),'MPE
G-4');
video.FrameRate=15;
open(video)
writeVideo(video,F)
close(video)
```


B. MATLAB CODES FOR THE ESTIMATION OF HYDRO-GEOMETRIC, HYDRODYNAMIC AND MIXING PARAMETERS OF RECEIVING WATER BODIES

In this appendix MATLAB ® codes for the estimation of hydro-geometric, hydrodynamic and mixing parameters from raw monitoring data are provided.

main.m

```
data_load;  
data_id;  
seas;  
width;  
xsec;  
q_est;  
velo;  
depth;  
pecno;  
tabul;
```

data_load.m

```
% *** initial statements ***

clear all;
clc;

% ** end of initial statements **

% *** load data ***
% can be replaced with and 'input' argument to
% ask from the user to provide relevant data.

load data_1;

slope=[0.005;0.0075;0.0195;0.0045;0.005;0.0125;0.003;
0.006;0.004;0.007;0.0055;0.0085;0.0030;0.01];

% ** end of load data **
```

data_id.m

```
% *** production of unique data numbers ***

g_id=t_no*100000000+s_id*100000+xm*100;
g_id_g=findgroups(g_id);
st_id=t_no*1000+s_id;
st_id_g=findgroups(st_id);
st_idvar=splitapply(@mean,st_id,g_id_g);
st_idvar_g=findgroups(st_idvar);

st_iduni=unique(st_id);
tno2=fix(st_iduni/1000);
st_iduni2=st_iduni-tno2*1000;
st_iduni3=unique(st_iduni2);
st_iduni2_g=findgroups(st_iduni2);

num_samp=zeros(numel(st_iduni3),1);
```

data_id.m (cont'd)

```
for i=1:numel(st_iduni3)
num_samp(i)=sum(st_iduni2==st_iduni3(i));
end

st_iduni3_gt1=st_iduni3(num_samp>1);

% ** end of id number production **
```

seas.m

```
% *** dry-wet season differentiation ***

n=numel(tno2);
m=numel(unique(tno2));
t_seas=string(zeros(n,1));
t_mo=month(datetime(t_ym,'InputFormat','MM-yyyy'));
t_mo2=string(zeros(m,1));

for i=1:n
    for j=1:m
        if t_mo(j)>5 && t_mo(j)<11
            t_mo2(j)="dry";
        else
            t_mo2(j)="wet";
        end
    end
    t_seas(i)=t_mo2(tno2(i));
end

clear n; clear m; clear i; clear j;

% ** end of dry-wet season differentiation **
```

width.m

```
% *** width calculation ***

wm=splitapply(@max,xm,st_id_g);

wm_=[splitapply(@mean,wm,st_iduni2_g)
splitapply(@min,wm,st_iduni2_g)
splitapply(@max,wm,st_iduni2_g)];

% ** end of width calculation **
```

xsec.m

```
% *** x-sectional area calculation ***

ysecm=splitapply(@max,ym,g_id_g);

xmvar=splitapply(@mean,xm,g_id_g);

yxm2=splitapply(@(x1,x2){yx(x1,x2)},ysecm,xmvar,st_idvar_g);
yxm2=cell2mat(yxm2);
am2=splitapply(@sum,yxm2,st_idvar_g);

am2_=[splitapply(@mean,am2,st_iduni2_g)
splitapply(@min,am2,st_iduni2_g)
splitapply(@max,am2,st_iduni2_g)];

% ** end of x-sectional area calculation **
```

yx.m (func)

```
function [z] = yx(y,x)
c=numel(y);
```

yx.m (func, cont'd)

```
for k=1:c
    if k==1
        z(k,1)=y(k)*x(k)/2;
    elseif k==c
        if y(k)==0
            z(k,1)=(y(k)+y(k-1))*(x(k)-x(k-1))/2;
        else
            z(k,1)=y(k)*(x(k)-x(k-1))/2;
        end
    else
        z(k,1)=(y(k)+y(k-1))*(x(k)-x(k-1))/2;
    end
end
end
```

q_est.m

```
% *** calculation of y interval values ***
% to be used in flowrate estimation

ydifm=splitapply(@ (x) {ydif(x)},ym,g_id_g);
ydifm=cell2mat(ydifm);

% ** end of y invernal value calculation **

% *** 1st step of flowrate calculation ***
% y invernal values calculated with ydif fucntion
% are multiplied with velocity values.

yvm2s=splitapply(@ (x1,x2) {yv(x1,x2)},ydifm,vms,g_id_g)
;
yvm2s=cell2mat(yvm2s);

% ** end of 1st step of flowrate calculation **
```

q_est.m (cont'd)

```
% *** 2nd step of flowrate calculation ***
% the values for each corresponding x interval are
summed up.

yvsumm2s=splitapply(@sum,yvm2s,g_id_g);

yvnz=~(yvm2s==0);
yv_nz=nonzeros(yvm2s);

vmsnz=vms(yvnz);
yv2m3s=vmsnz.*yv_nz;
stid_nz=st_id(yvnz);
stidnz_g=findgroups(stid_nz);
yv2summ3s=splitapply(@sum,yv2m3s,stidnz_g);
yvnz_sum=splitapply(@sum,yv_nz,stidnz_g);

% ** end of 2nd step of flowrate calculation **

% *** 3rd step of flowrate calculation ***
% x value intervals are found and the values
calculated in step 2
% are multiplied by these x values to get preliminary
results for
% flowrate calculation. then these preliminary values
are summed up
% to get the actual flowrate values in m^3/h for each
station
% during each monitoring period.

yvxm3s=splitapply(@(x1,x2){yv(x1,x2)},yvsumm2s,xmvar,
st_idvar_g);
yvxm3s=cell2mat(yvxm3s);

qm3s=splitapply(@sum,yvxm3s,st_idvar_g);

qm3s_=[splitapply(@mean,qm3s,st_iduni2_g)
splitapply(@min,qm3s,st_iduni2_g)
splitapply(@max,qm3s,st_iduni2_g)];

% ** end of step 3 of flowrate calculation **
```

ydif.m (func)

```
function [y_m] = ydif(ym)
c=numel(ym);
for k=1:c
    if k<c
        y_m(k,1)=ym(k)-ym(k+1);
    else
        y_m(k,1)=ym(k);
    end
end
end
```

yv.m (func)

```
function [z] = yv(y,v)
c=numel(y);
for k=1:c
    if k<c
        z(k,1)=(v(k)+v(k+1))*y(k)/2;
    else
        z(k,1)=y(k)/2*v(k);
    end
end
end
```

yvx.m (func)

```
function [z] = yvx(yv,x)
c=numel(yv);
for k=1:c
    if k==1
        z(k,1)=yv(k)*x(k)/2;
    elseif k==c
        if yv(k)==0
            z(k,1)=(yv(k)+yv(k-1))*(x(k)-x(k-1))/2;
        else
            z(k,1)=yv(k)*(x(k)-x(k-1))/2;
        end
    else
        z(k,1)=(yv(k)+yv(k-1))*(x(k)-x(k-1))/2;
    end
end
end
```

velo.m

```
% *** velocity calculations ***3

u1=qm3s./am2;
u1_=[splitapply(@mean,u1,st_iduni2_g)
splitapply(@min,u1,st_iduni2_g)
splitapply(@max,u1,st_iduni2_g)];

u2=yv2summ3s./yvnz_sum;
u2_=[splitapply(@mean,u2,st_iduni2_g)
splitapply(@min,u2,st_iduni2_g)
splitapply(@max,u2,st_iduni2_g)];

u=[u1 u2];
u_=[u1_ u2_];

% ** end of velocity calculations **
```

depth.m

```
% *** average depth calculation ***

h2=qm3s./u2./wm;
h3=splitapply(@mean,ysecm(~(ysecm==0)),findgroups(st_idvar(~(ysecm==0))));

h2_=[splitapply(@mean,h2,st_iduni2_g)
splitapply(@min,h2,st_iduni2_g)
splitapply(@max,h2,st_iduni2_g)];
h3_=[splitapply(@mean,h3,st_iduni2_g)
splitapply(@min,h3,st_iduni2_g)
splitapply(@max,h3,st_iduni2_g)];

h=[h2 h3];
h_=[h2_ h3_];

% ** end of average depth calculation **
```

pecno.m (for the estimation of vertical, transverse, and longitudinal dispersion coefficients, vertical and transverse characteristic mixing distances and Peclet numbers)

```
dx=zeros(numel(h3),1);
dy=dx;
ustar=dx;
ept0=dx;

w_h=wm./h3;
w_h_=w_h(:,1)./h3_(:,1);

for i=1:numel(h3)

ustar(i)=sqrt(9.81*h3(i)*slope(st_iduni3==st_iduni2(i)));

ept0(i)=0.145+(1/3520)*u2(i)/ustar(i)*(wm(i)/h3(i))^1.38;
```

pecno.m (cont'd)

```
dx(i)=0.15/8/ept0(i)*(wm(i)/h3(i))^(5/3)*(u2(i)/ustar(i))^2*h3(i)*ustar(i);

    dy(i)=ept0(i)*h3(i)*ustar(i);

end

clear i;

ustar_=sqrt(9.81*h3_(:,1).*slope);

ept0_=0.145+(1/3520).*u2_(:,1)./ustar_.*(wm_(:,1)./h3_(:,1)).^1.38;

dx_=0.15./(8.*ept0_).*((wm_(:,1)./h3_(:,1)).^(5/3)).*(u2_(:,1)./ustar_).^2).*h3_(:,1).*ustar_(:,1);

dy_=ept0_.*h3_(:,1).*ustar_;

ly_rb=(wm.^2).*u2./(12.5*dy);
ly_cl=((wm./2).^2).*u2./(12.5*dy);

dz=0.067*h3.*ustar;
lz1=12*h3;
lz2=h3.^2.*u2./(12.5*dz);

ly_rb_=((wm_(:,1)).^2).*u2_(:,1)/(12.5*dy_);
ly_cl_=((wm_(:,1))./2).^2).*u2_(:,1)/(12.5*dy_);

dz=0.067.*h3_(:,1).*ustar_;
lz1_=12*h3_(:,1);
lz2_=h3_(:,1).^2.*u2_(:,1)/(12.5*dz_);

peclet_ly_rb=u2.*ly_rb./dx;
peclet_ly_rb_=u2_(:,1).*ly_rb_./dx_;
peclet_ly_cl=u2.*ly_cl./dx;
peclet_ly_cl_=u2_(:,1).*ly_cl_./dx_;
```

tabul.m (for the generation of tables from the processed data)

```
t_ym2=string(datetime(datetime(t_ym,'InputFormat','MM-
yyyy'),'Format','yyyy-MM'));
t_ym2_lar=string(zeros(numel(tno2),1));
slope_lar=zeros(numel(st_iduni3),1);
for i=1:numel(tno2)
t_ym2_lar(i)=t_ym2(tno2(i));
slope_lar(i)=slope(find(st_iduni3==st_iduni2(i)));
end

T_lar=table(st_iduni2,tno2,t_ym2_lar,slope_lar,wm,u2,h
3,w_h,am2,qm3s,...

ustar,dx,dy,dz,ly_rb,ly_cl,lz1,lz2,peclet_ly_rb,peclet
_ly_cl);
T_lar.Properties.VariableNames={'Station_ID','Tour_No'
,'Tour_Date',...

'Slope','Width_m','Velo_ms','Dep_m','Width_per_depth',
...

'A_m2','Q_m3s','ustar','Dx_Deng','Dy_ept0','Dz','Ly_Rb
','Ly_Cl',...
'Lz_1','Lz_2','Pec_No_LyRb','Pec_No_LyCl'};
T_sma=table(st_iduni3,num_samp,slope,wm_(:,1),wm_(:,2)
,wm_(:,3),...

u2_(:,1),u2_(:,2),u2_(:,3),h3_(:,1),h3_(:,2),h3_(:,3),
w_h_,...

am2_(:,1),am2_(:,2),am2_(:,3),qm3s_(:,1),qm3s_(:,2),qm
3s_(:,3),...

ustar_,dx_,dy_,dz_,ly_rb_,ly_cl_,lz1,lz2,peclet_ly_rb_,
peclet_ly_cl_);
T_sma.Properties.VariableNames={'Station_ID','Tot_Samp
_No','Slope',...

'Width_m_mean','Width_m_min','Width_m_max','Velo_ms_me
an',...

'Velo_ms_min','Velo_ms_max','Dep_m_mean','Dep_m_min','
Dep_m_max',...}
```

tabul.m (cont'd)

```
'Width_per_depth','A_m2_mean','A_m2_min','A_m2_max',...  
.  
'Q_m3s_mean','Q_m3s_min','Q_m3s_max','ustar','Dx_Deng'  
,...  
  
'Dy_Ept0','Dz','Ly_Rb','Ly_Cl','Lz_1','Lz_2','Pec_No_L  
yRb','Pec_No_Ly_Cl'};  
  
writetable(T_lar,'tables\pre_lar.csv');  
writetable(T_sma,'tables\pre_sma.csv');  
  
clear i;
```