HEALTH RISK ASSESSMENT FOR THE LAND APPLICATION OF BIOSOLIDS IN ANKARA, TURKEY

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HEALTH RISK ASSESSMENT FOR THE LAND APPLICATION OF BIOLSOLIDS IN ANKARA TURKEY: INGESTION PATHWAY

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ABSTRACT

HEALTH RISK ASSESSMENT FOR THE LAND APPLICATION OF BIOSOLIDS IN ANKARA, TURKEY: INGESTION PATHWAY

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Biosolids are valuable products which can be beneficially used in land application. However, the possibility of serious health effects on humans due to several pollutants in biosolids creates a big concern. To address this issue, risk-based methodologies are commonly used to evaluate health effects associated with the land application of biosolids. This study aims to investigate the health risks associated with ingestion of biosolids or soil mixed with biosolids by a child. This study is the first health risk assessment study in Turkey for land application of biosolids. Monthly sludge samples taken from Ankara Central Wastewater Treatment Plant (ACWWTP) in 2012 were analyzed for seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn), and two organic contaminants (PCB and NPE) concentrations. To calculate health risks, methodologies developed by U.S. Environmental Protection Agency (U.S. EPA) and French National Institute for Industrial Environment and Risks (INERIS) were used. With both methods, cancer and non-cancer risks for the ingestion by a child pathway were determined and found to be below the acceptable cancer and non-cancer risk levels suggested by U.S. EPA and INERIS. Additionally, same health risk calculations were conducted for sludge and soil limit values provided in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010) to determine what the maximum health risk would be for the worst case scenario in Turkey. According to the results, even if the concentrations are at the maximum possible regulatory levels, the health risks are still low.

Keywords: Biosolids, Land Application, Health Risk, Ingestion Pathway

ÖZ

ANKARA'DA (TÜRKİYE) BİYOKATILARIN TARIM UYGULAMALARI IÇIN SAĞLIK RİSKİ DEĞERLENDİRMESİ: YUTMA YOLU

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Biyokatılar tarım alanlarında yararlı bir şekilde kullanılabilen değerli ürünlerdir. Ancak, birtakım kirleticilerin biyokatılarda bulunma olasılığı nedeniyle, bu kirleticilerin insan sağlığına ciddi etkileri büyük bir endişe teşkil etmektedir. Bu sorunu ele almak amacıyla, biyokatıların tarımsal kullanımıyla ilişkili sağlık etkilerini değerlendirmek için risk bazlı yöntemler yaygın bir şekilde kullanılmaktadır. Bu çalışma biyokatıların ya da biyokatılarla karıştırılan toprağın çocuk tarafından yutulmasıyla ilişkili sağlık risklerini incelemeyi amaçlamaktadır. Bu çalışma, Türkiye'de biyokatıların tarım alanlarında kullanılması için yapılan ilk sağlık riski değerlendirmesi çalışmasıdır. Biyokatı örnekleri Ankara Merkez Atıksu Arıtma Tesisi'nden 2012 yılında aylık olarak alınmıştır ve yedi ağır metal (Cd, Cr, Cu, Hg, Ni, Pb ve Zn), ve iki organik kirletici (PCBs ve NPEs) konsantrasyonları analiz edilmiştir. Sağlık risklerini değerlendirmek için ABD Çevre Koruma Ajansı (U.S. EPA) ve Fransız Ulusal Enstitüsü Endüstriyel Çevre ve Riskler Birimi (INERIS) tarafından geliştirilen yöntemler kullanılmıştır. İki yöntem ile de çocuk tarafından yutulması maruz kalma yolu için kanser ve kanser olmayan riskler, U.S. EPA ve INERIS'in önerdiği kabul edilebilir kanser ya da kanser olmayan risk seviyelerine göre düşük olarak bulunmuştur. Ek olarak, Türkiye'de en kötü koşulda, en fazla sağlık riskinin ne olacağının belirlenmesi için, Evsel ve Kentsel Arıtma Çamurların Toprakta Kullanılmasına Dair Yönetmelik (2010) kapsamında sağlanan arıtma çamuru ve toprak sınır değerleri için aynı sağlık riski hesaplamaları yapılmıştır. Elde edilen sonuçlara göre, konsantrasyonlar muhtemel en fazla yönetmelik seviyelerinde olsa bile, sağlık risklerinin hala düşük olduğu belirlenmiştir.

Anahtar Kelimeler: Biyokatılar, Sağlık Riski, Tarımsal Uygulama, Yutma Yolu

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CHAPTER 1

INTRODUCTION

Sewage sludge is the solid, semisolid, or liquid residue generated during treatment of sewage (U.S. EPA, 2002). As the amount of treated wastewater has increased in the world, the amount of sewage sludge production has also increased and different disposal routes have come into effect. Thirty years ago, ocean disposal was considered as the common method for sludge disposal. However, after ocean disposal of sewage sludge was banned worldwide, other alternatives such as landfilling, incineration and land application were taken into consideration. Along with the development of beneficial use alternatives, new terminology for sewage sludge was also introduced to fix the bad image and to promote the beneficial use of sewage sludge. The sewage sludge that has gone through proper stabilization processes and which has high quality can be beneficially recycled. For this type of sludge the term 'biosolids' was started to be used in wastewater industry and adapted by U.S. EPA. Due to this reason in addition to the term 'sludge', the term 'biosolids' can also be seen in books and other references.

According to the economic status, available infrastructure, and quality of sludge, countries apply different disposal alternatives for sludge. Land application is one of the most commonly used disposal routes. Sludge can be used beneficially on land due to its organic matter and nutrient content. Agricultural lands, grazing land and forests are some of the application areas for sludge. Land application of sludge has many advantages on the quality of soil and crop. In addition, it is an economical alternative since it can be used instead of expensive chemical fertilizers.

Even though sludge has many benefits; it may contain several inorganic, organic and biological pollutants. As a result, use of sludge on land may lead to potential risks for human health and the environment. In order to prevent adverse effects of land application of sludge, some countries established regulations for the use on land. Turkey also has a regulation named 'Regulation for the Use of Sewage Sludge in Agriculture' which has been in application since 2010. The main aim of these regulations is to set limit values and provide management standards for pollutants in sludge in order to protect public and environmental health.

To set limit values for land application of sludge or to determine potential adverse effects before application, risk assessment studies are commonly applied throughout the world. U.S. EPA conducted an extensive study to determine risk-based pollutant limits for heavy metals and established 40 CFR Part 503 Rule. This regulation has heavy metal pollutant limits, pathogen limits and operational standards, and management practices for land application of biosolids. French National Institute for Industrial Environment and Risks (INERIS) and the Norwegian Scientific Committee for Food Safety (VKM) also assessed extensive studies associated with possible risks for public health due to land application of sludge.

In Turkey, land application of sludge is not a very common disposal route and it should be evaluated in terms of its benefits on soil and crop quality and economical value. However, in order to provide safe use of sludge on land and provide valuable information for decision makers, health risks originating from the application of biosolids need to be known. In Turkey, health risks due to land application of sludge are not well-known and health risk assessment studies related to land application have not been conducted yet.

The aim of this study is to investigate possible health risks associated with land application of sludge samples from Ankara Central Wastewater Treatment Plant (ACWWTP) through ingestion pathway. This study is the first example of health risk assessment study associated with land application of sludge in Turkey. The findings from this study will provide valuable information in terms of possibility of land application of sludge samples from ACWWTP and will serve as a model for future

health risk assessment studies related to land application in Turkey.

In this study, seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn), and two organic chemicals (PCB, and NPE) were analyzed in monthly sludge samples collected from ACWWTP. The results were compared with pollutant limit values provided in Turkish Regulation for the Use of Sewage Sludge in agriculture, in terms of possibility of the use of this sludge in land application. After that, the pollutant concentrations measured in sludge samples were used in health risk calculations associated with land application of biosolids through ingestion pathway. For health risk calculations, methodologies developed by U.S. EPA and INERIS were used. With the available data and assumptions, health risk calculations were done and the results were discussed in terms of possible adverse health effects.

CHAPTER 2

LITERATURE REVIEW

2.1. Definitions of Sewage Sludge and Biosolids

Sewage sludge is one of the constituents produced during wastewater treatment plant processes. It is defined by U.S. EPA as 'the solid, semi-solid, or liquid by-product generated during the treatment of wastewater at sewage treatment plants' (U.S. EPA, 2002). In order to distinguish raw sludge from processed sludge which can be used in land application, the term 'biosolids' was first used in wastewater treatment industry. After then, the term was adopted by U.S. EPA for high quality sewage sludge which is not raw and do not contain large amount of pollutants (Jacobs and McCreary, 2001) and defined as 'the primarily organic solid product yielded by municipal wastewater treatment processes that can be beneficially recycled' (National Research Council, 2002).

2.2. Components of Sludge

Type of wastewater treatment and the quality of wastewater are the main factors affecting the quality and quantity of sludge (Sanin *et al*., 2011). Generally, sludge contains 40-80% organic matter in dry weight and loading is mostly due to human fecal matter (Schowanek *et al*., 2004). In addition to organic matter, it also includes plant nutrients (nitrogen and phosphorus), macronutrients (calcium, potassium, and sulphur) and micronutrients (copper and zinc) (European Commission, 2008).

Sludge may also include pollutants from mixture of organic, inorganic and biological contaminants from domestic, commercial, and industrial wastewater and formed compounds during the wastewater treatment processes. Metals and trace elements, PCB's, dioxins, steroids, pharmaceuticals are among the contaminants found in sewage sludge (National Research Council, 2002). Furthermore, PAHs, solvents, flame retardants, plasticizers, detergents, pesticides, and personal care products are the other contaminants that can be detected in sewage sludge (European Commission, 2008;Singh and Agrawal, 2007).Apart from inorganic and organic pollutants, disease causing organisms, which are called pathogens and vectors are also present in sewage sludge as well (U.S. EPA, 1994a).

2.3. Quantities of Sludge

In the past 30 years, the main aim for wastewater treatment has been centered upon the enhancement of the effluent quality of wastewater with the advanced treatment methods. Use of advanced wastewater treatment technologies has increased the production of solids and biosolids (Tchobanoglous *et. al*., 2003).

Around the world, the amount of sludge production has been observed in huge amounts. In U.S., 6.2 million tons of sludge was produced in 2004 (UN-HABITAT, 2008). According to European Commission (2008), approximately 10 million tons of sludge in dry matter was produced between 2003 and 2006 in EU. The production of sludge has been increased over the last 20 years in some EU member states due to implementation of Urban Wastewater Treatment Directive. On the other hand, in some state members such as Germany and Denmark, the amount of sludge production has been stabilized or decreased due to decrease in water consumption and use of advance technologies in sludge treatment.

In Turkey, according to Öztürk (2010), in 2008, around 1.1 million tons dry matter (DM) of sludge was produced in Turkey and the amount of biosolids production has been increasing in the following years (Figure 2.1).

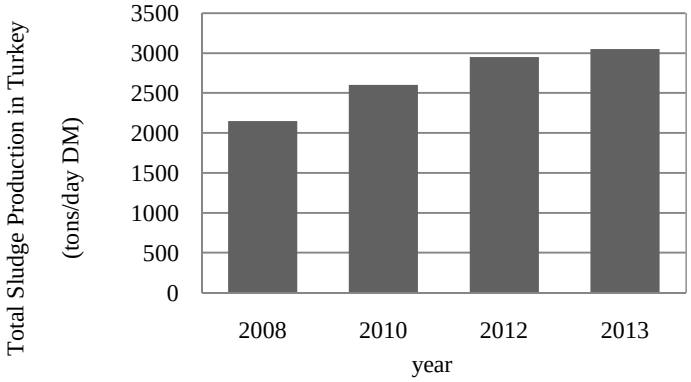

Figure 2.1: Total Sludge Production in Turkey (Öztürk, 2010)

2.4. Management of Sludge

Sludge produced in wastewater treatment plants is a big concern in terms of quality and quantity. Sludge has high water and organic matter content. It also includes several organic and inorganic contaminants, pathogens and vector attraction potential. The quality of sludge is the most important factor that affects the ultimate disposal route of sludge. Sludge can be disposed of with different routes. However, to be suitable for ultimate disposal, treatment processes are applied to sludge (Wang *et al.*, 2008; Tchobanoglous *et al.*, 2003).

In the following sections, main treatment processes for sludge and its disposal and beneficial use are discussed in detail.

2.4.1. Treatment of Sludge

Sludge can be treated with several different types of processes. Thickening, stabilization, conditioning, and dewatering are the four main sludge treatment processes operated in wastewater treatment plants to meet economical and regulatory requirements (Wang *et al.*, 2008; Tchobanoglous *et al.*, 2003).

Thickening is generally the first process in sludge treatment. It aims to reduce volume by the removal of water from sludge. Volume reduction is required for the reduction of size of tanks and pipes required for downstream sludge treatment, amount of chemicals used in conditioning and operational costs of treatment plants (McFarland, 2001; Tchobanoglous *et al.*, 2003). Gravity thickening, dissolved air floatation thickening, centrifugal thickening, gravity-belt thickening, and rotary drum thickening are the major thickening processes used in sludge treatment (McFarland, 2001).

Stabilization provides pathogen and vector attraction reduction, odor elimination, and reduction in putrefaction (Wang *et al.*, 2008). Additionally, volume reduction of sludge, methane gas production and dewaterability improvement can also be achieved by stabilization (Tchobanoglous *et al.*, 2003).Stabilization processes can be biological, chemical or thermal (Andreoli *et al.*, 2007).Alkaline stabilization, anaerobic digestion, aerobic digestion, and composting are the main stabilization processes used in wastewater treatment plants (Tchobanoglous *et al.*, 2003).

Stabilization is especially important for land application of sludge beneficially. In order to reduce health risks due to pathogens and vector attraction potential in sludge, before land application, stabilization should be applied (Andreoli *et al.*, 2007).

Conditioning is mainly used to increase dewaterability of sludge. Applying conditioning before dewatering process increases the capacity of water removal and solids capture (McFarland, 2001). Physical, chemical and biological conditioning processes can be applied in sludge treatment (Wang *et al.*, 2008).

Dewatering is applied in order to decrease the moisture content of the sludge. Dewatering reduces transportation costs of sludge to the ultimate disposal site. In addition, dewatering enhances the calorific value of sludge which is important for incineration and prevents leachate production after landfilling of sludge (Tchobanoglous *et al.*, 2003). Belt filter press and centrifugation are the most commonly used processes in sludge dewatering. Furthermore, drying processes can be also used in order to decrease the moisture content of sludge. Drying beds and thermal drying are the main processes used in sludge treatment (Andreoli *et al.*, 2007).

2.4.2. Disposal and Beneficial Use of Sludge

The disposal of sludge in a safe way is an important environmental concern in the world (Singh, 2007). In the past, ocean/sea dumping of sludge was considered as a common disposal route and 20 million tons of sludge had been disposed by this method annually in 1980s (Laturnus *et al*., 2007). Sea/Ocean disposal of sludge was banned in U.S. by 'Ocean Dumping Ban Act, 1988'due to adverse effects on quality of water and ecosystems (U.S. EPA, 2012).In addition, '1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972', was established in 1996 to prevent ocean/sea disposal of sludge. The convention has been accepted by 42 countries throughout the world so far (International Maritime Organization, 2013). Since the ban on sea/ocean disposal, other disposal methods such as landfilling, incineration and land applications began to be applied throughout the world (Laturnus *et al*., 2007). Each country has different sludge disposal priorities (Table 2.1)

Table 2.1: Sludge Disposal Alternatives in the World (%) (European Commission, 2008; Laturnus *et al.*, 2007;UN-HABITAT, 2008)

	Agriculture	Landfill	Incineration	Other
Austria	15	50	35	-
Canada (Western)	66	4	0	30
China	45	34.5	3.5	17
Denmark	55	2	43	-
Finland	12	6	-	80
Greece	-	-	>90	
Germany	30	3	38	29
Ireland	63	35	-	3
Italy	32	37	8	22
Netherlands	47	-	20	33
Poland	14	87	-	7
Sweden	10-15	-	2	85-90
UK	64	1	19.5	15.5
U.S.A.	41	17	22	10

In Turkey, the most common disposal route for sludge is landfilling (UN-HABITAT, 2008). However, due to beneficial contents of sludge and poor soil conditions in Turkey, there is a potential for agricultural use (UN-HABITAT, 2008). From this point onwards, the main emphasis will be placed on land application due to the aim of this study being the risks originating from the land application of biosolids.

2.4.2.1. Land Application of Sludge

Land application is defined by U.S. EPA (1994b) as "the spreading, spraying, injection, or incorporation of sewage sludge, including materials derived from sewage sludge (e.g., compost and pelletized sewage sludge), onto or below the surface of the land to take advantage of the soil enhancing qualities of the sewage sludge". Biosolids can be used in agricultural land, forests, and rangelands or on disturbed land in need of reclamation (U.S. EPA, 2000).

Land application of sludge provides many benefits for soil and crop. It is a source for nitrogen and phosphorus which increases crop production. Organic matter in sludge enhances water infiltration, water holding capacity of soil, and soil granulation (Jacobs and McCreary, 2001). Additionally, land application of sludge decreases soil compaction and erosion of soil. It also has benefits for living organisms in soil and plants such as being a source for energy and nutrients (Jacobs and McCreary, 2001). Furthermore, as an economical point of view, it can be substituted for expensive chemical fertilizers (Wang *et al*., 2009).

Although sludge has several benefits for soil quality and crop production, it can pose potential health risks to human and ecological receptors such as animals, plants, and organisms since it contains metals and trace elements, PCB's, dioxins, steroids, pharmaceuticals, pathogens, bacteria, viruses, and disease vectors (National Research Council, 2002). The pollutants may result in contamination of the environment and this lead to consideration of potential health and safety implications in order to prevent adverse effects (World Health Organization, 2004).

2.4.2.2. Regulations on Land Application of Sludge

Many countries have different regulations associated with land application of sludge. In U.S.A, EPA established 40 CRF Part 503 Rule on February, 19, 1993 under the Clean Water Act (CWA). The rule is composed of five subparts:

- Subpart A: General provisions, Applicability and Purpose etc.
- Subpart B: Requirements for Land Application
- Subpart C: Requirements for Surface Disposal
- Subpart D: Requirements for Pathogen and Vector Attraction Reduction
- Subpart E: Requirements for Incineration

The subparts of Part 503 Rule mainly include management practices, pollutant limits for metals and technology-based operational standards for pathogens to protect public health and the environment. In addition, general requirements, reporting, monitoring, recordkeeping, operational standards for total hydrocarbons or carbon monoxide and pathogen and vector reduction are also included (Figure 2.2).

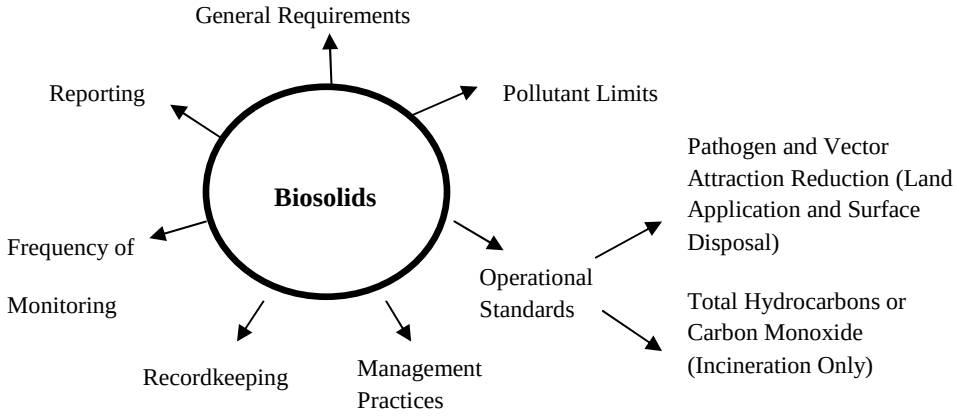

Figure 2.2: Elements of Part 503 Rule (U.S. EPA, 1994a)

In the Part 503 rule, risk assessment for biosolids is conducted for three disposal methods: land application, surface disposal and incineration to determine risk-based pollutant limits. In land application, heavy metals found in biosolids applied to the land must meet risk-based pollutant limits whereas operational standards are applied for pathogens and vectors (U.S. EPA, 1995). However, for trace organic pollutants such as PCBs, PAH etc., there are no limit values in Part 503 Rule. These chemicals were evaluated in risk assessment; however, they were eliminated due to the following three findings: ban on use of these chemicals in U.S.A, their low percentages in sewage sludge, and lack of available data (Harrison *et al*., 2006).

In EU, the Sewage Sludge Directive (86/278/EEC) was established in 1986 to increase the use of sewage sludge in agriculture and to avoid detrimental effects on environment and human health. The Directive was prepared using available data in 1980s and COST 68 program for determination of risks. It includes limit values for heavy metals in sludge and soil to be treated with sludge. After establishment, EU countries adopted this directive; and some countries implemented stricter limit values for heavy metals and included organic pollutants which are not included in the directive (EU, 2008). After 86/278/EEC, a draft document (Working Document on Sludge, 3rd Draft) was prepared in 2000 for the use of sludge for agricultural purposes. It includes additional organic pollutant limit concentrations for sludge to be applied to land different from 86/278/EEC and new proposed heavy metal limit concentrations (European Commission, 2000). However, this draft document has not been accepted as the new directive yet.

In Turkey, Regulation for the Use of Sewage Sludge in Agriculture was put into force on August, 3, 2010.It aims to take necessary precautions for the use of sewage sludge in soil in a manner to determine compliance with the objectives of sustainable development. It covers technical and administrative procedures for controlled use of sewage sludge in soil without any harmful effects on humans, animals, and plants (Regulation for the Use of Sewage Sludge in Agriculture, 2010).

Table 2.2 and Table 2.3 provide the comparison of limit values for heavy metals and organic pollutants in various regulations in U.S., Europe and Turkey. As can be seen from Table 2.2, for heavy metals, stricter limit values are included in the Netherlands except for Cadmium (Cd). The strictest value for Cd belongs to the regulation of Denmark. Arsenic (As) and Selenium (Se) are only included in U.S. regulation (Part 503 Rule). For organic pollutants, U.S. EPA Part 503 Rule and 86/278/EEC do not have any limit values. However, Turkish Regulation and Working Document on Sludge 3rd Draft have the same limit values for organic pollutants. Additionally, as an EU member, France has limit values only for three organic pollutants and Denmark has limit values for four organic pollutants.

Table 2.2: Heavy Metal Limit Values (mg pollutant/kg biosolids DW)for Land Application of Biosolids in the World (European Commission, 2000; European Commission, 2008; U.S. EPA, 1995; Regulation for the Use of Sludge in Agriculture, 2010)

Heavy Metals	U.S.	EU 86/278/EEC	EU Working Document on Sludge, 3rd Draft	Turkey	France	Denmark	Netherlands
As	41	-	-	-	-	25	15
Cd	39	20-40	10	10	20	0.8	1.25
Cr	-	-	1000	1000	1000	100	75
Cu	1500	1000-1750	1000	1000	1000	1000	75
Hg	17	16-25	10	10	10	0.8	0.75
Mo	-	-	-	-	-	-	-
Ni	420	300-400	300	300	200	30	30
Pb	300	750-1200	750	750	800	120	100
Se	100	-	-	-	-	-	-
Zn	2800	2500-4000	2500	2500	3000	4000	300

-: Not included

Table 2.3: Organic Pollutants Limit Values (mg pollutant/kg biosolids DW) for Land Application of Biosolids in the World (European Commission, 2000; European Commission, 2008; U.S. EPA, 1995; Regulation for the use of sludge in agriculture, 2010)

Organic Pollutants	U.S.	EU 86/278/EEC	EU Working Document on Sludge, 3rd Draft	Turkey	France	Denmark
AOX[1]	-	-	500	500	-	-
DEHP[2]	-	-	2600	2600	-	50
LAS[3]	-	-	100	100	-	1300
NP/NPE[4]	-	-	50	50	-	10
PAH[5]	-	-	6	6	Fluoranthene: 4 Benzo(b)fluoranthene:2.5 Benzo(a)pyrene: 1.5	3
PCB[6]	-	-	0.8	0.8	0.8	-
PCDD/F[7]	-	-	100 (ng toxic equivalent (TE)/kg DW)	100 (ngtoxic equivalent (TE)/ kg DW)	-	-

-: Not included
[1] *Sum of halogenated organic compounds.*
[2] *Di(2-ethylhexyl)phthalate*
[3] *Linearalkylbenzenesulphonates.*
[4] *Nonylphenoland nonylphenolethoxylates with 1 or 2 ethoxy groups*
[5] *Sum of the following polycyclic aromatic hydrocarbons: acenapthene, phenanthrene, fluorene,flouranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1, 2, 3 c,d)pyrene.*
[6] *Sum of congeners 28, 52,101,118,138,153 and 180*
[7] *Polychlorinated dibenzodioxins/ dibenzofuranes*

Apart from the limit values for biosolids, there are limit values for heavy metals in soil in order for proper land application with different pH values in EU and Turkish Regulation (Table 2.4). In U.S. Regulation, there are no soil based pollutant limits for land application of biosolids.

Table 2.4: Limit Values for Heavy Metals in Soil (mg pollutant /kg dry soil) for Land Application of Biosolids (European Commission, 2000; Regulation for the Use of Sewage Sludge in agriculture, 2010)

Heavy Metals	EU (86/278/EEC) 6<pH<7	EU (Working Document on Sludge, 3rd Draft) 5≤pH<6	EU (Working Document on Sludge, 3rd Draft) 6≤pH<7	EU (Working Document on Sludge, 3rd Draft) pH≥7	Turkey 6≤pH<7	Turkey pH≥7
Cd	1 to 3	0.5	1	1.5	1	1.5
Cr	-	30	60	100	60	100
Cu	50 to 140	20	50	100	50	100
Hg	1 to 1.5	0.1	0.5	1	0.5	1
Ni	30 to 75	15	50	70	50	70
Pb	50 to 300	70	70	100	70	100
Zn	150 to 300	60	150	200	150	200

2.5. Health Effects of Pollutants Present in Sludge on Humans

Possible health effects (carcinogenic and non-carcinogenic) of the specified pollutants in biosolids should be known before land application. Within the scope of this study, health risk assessment for seven heavy metals (cadmium, chromium, copper, lead, mercury, nickel, and zinc) and two organic pollutants (PCBs and selected NPEs) are conducted and provided in Section 3.2. Thus, in this section, health effects of these selected pollutants are discussed in detail.

2.5.1. Health Effects of Heavy Metals on Humans

Heavy metals enter wastewater treatment systems by domestic, industrial, commercial, and urban runoff sources. The majority of heavy metals are retained in sewage sludge during wastewater treatment processes (EU Commission, 2001). When sewage sludge is applied to land as a disposal method, heavy metal content in sewage sludge may pose adverse health effects on humans. Each heavy metal has different acute, chronic or carcinogenic health effects in different doses of exposure.

Cadmium (Cd): Cadmium is not an essential element for humans and may have toxic effects. Domestic sources such as rechargeable batteries, paints, food products, detergents, body care products, and photography are the main sources for cadmium contamination in sewage sludge. In addition, launderettes, small electroplating, coating shops, and plastic manufacturing are the commercial sources of cadmium (EU Commission, 2001).

Some acute and chronic health effects can be seen after cadmium exposure. Acute health effects may be seen as cough, shortness of breath, digestive tract irritation, colitis, vomiting, and pulmanory edema followed by bronchopneumonia. For chronic health effects, kidney, liver and testicle damage, hypertension, respiratory effects, carbohydrate metabolism, teratogenesis, anaemia, softening of the bones, osteoporosis, and “itai-itai” or “ouch-ouch” disease resulting in bone pains are the possible effects after exposure to cadmium (Epstein, 2003; European Commission, 2001; World Health Organization, 2010).

For carcinogenic effects, cadmium is classified as Group B1 (See Appendix A) by U.S. EPA. There is limited data for human carcinogenicity for inhalation. Lung cancer was observed in some studies for cadmium smelter workers (U.S. EPA Integrated Risk Information System (IRIS), 2012). In addition, prostate cancer is observed due to exposure to cadmium in some studies. However, the evidence is weak (U.S. EPA, 1985). Except for inhalation exposure, the data is inadequate for oral exposure (U.S. EPA IRIS, 2012).

Chromium (Cr): In biosolids, the chromium is found as Cr (III). It is essential for humans and animals for lipid, protein, and fat metabolism. Moreover, it is important for insulin action in peripheral tissue (U.S. EPA IRIS, 2012). The sources of chromium in sewage sludge are diffuse sources such as preservatives, dying and tanning in leather processing (European Commission, 2001).

The data is limited on non-carcinogenic effects of Cr (III) in humans. There are no studies for reproductive and developmental effects in humans (U.S. EPA, 1998) and very limited data indicate respiratory tract and renal effects of Cr (III) (U.S. EPA, 1998).

As data on non-carcinogenic effects, the animal and human data is inadequate for the carcinogenicity of Cr (III). There are studies performed for inhalation exposure; however, data is inadequate for determination of carcinogenicity of Cr (III) on humans. In addition, the animal data obtained from studies for oral and inhalation exposure routes does not provide a sufficient determination of carcinogenicity of Cr (III). So, Cr (III) is classified as in Group D (See Appendix A) (U.S. EPA IRIS, 2012).

Copper (Cu): Copper is also an essential micronutrient for humans. However, some adverse effects can be seen when excess or deficient amounts of copper are in human body. Copper contamination is mainly due to corrosion and leaching of plumbing, paints, fungicides and wood preservatives. In

addition, electronic, plastics, plating, paper, textile, printing industry are also main sources (EU Commission, 2001).

After single oral exposure of copper, metallic taste, epigastric pain, headache, nausea, dizziness, vomiting, haematuria, massive gastrointestinal bleeding, liver and kidney damage, and death have been reported (International Programme on Chemical Safety, 1998). Kidney and liver damage can also be seen due to long term (chronic) exposure. In addition, in high levels of exposure, anemia can be seen (New Hampshire Department of Environmental Services, 2005).

For carcinogenic effects, no human data is available and animal data is inadequate to determine carcinogenicity of copper (U.S. EPA IRIS, 2012). U.S. EPA classifies carcinogenicity of copper in Group D (See Appendix A) (New Hampshire Department of Environmental Services, 2005).

Lead (Pb): Lead may enter wastewater treatment processes by old piping systems, old paints, batteries, solder, cable covering and PVC piping (EU Commission, 2001).Lead has adverse effects such as neurotoxicity, developmental delays, impaired hearing acuity, impaired hemoglobin synthesis, increase in blood pressure, decrements in glomerular filtration rate, colic (abdominal pain, cramps, nausea, vomiting etc.), male reproductive impairment, effect on kidney functions and mortality due to cerebrovascular disease in long term exposure (on lead workers) (U.S. EPA IRIS, 2012; U.S. EPA, 2007a). In addition, some neurodevelopmental effects, musculosketal effects, hepatic effects, and renal effects may also be seen.

Lead mostly affects children due to their hand-to-mouth behavior. The exposure risk is very high for children (U.S. EPA, 2007a). Neurological effects such as dizziness, malaise, forgetfulness, and headache are seen in children. In addition, lead exposure may change hematological system. It may results in skeletal maturation, occurrence of dental caries and periodontal bone loss on children (U.S. EPA, 2007a).

Lead is classified in Group B2 (See Appendix A) since there is sufficient animal evidence. Increase in renal tumors was observed in studies on rats. However, human evidences are not adequate. All related studies on humans do not have exposure information and dose-response relationships (U.S. EPA IRIS, 2012).

Mercury (Hg): Mercury is a toxic and nonessential element for humans. In biosolids, mercury is assumed to be in the form of mercuric chloride ($HgCl_2$) (National Research Council, 2002)**.** Mercury can be included in thermometers, dental practices, old paints and pesticides, caustic soda solutions, wood preservatives, electrical equipment production and finally transferred to sewage sludge (EU Commission, 2001).

Mercury has non-cancer effects on humans. As acute effects, skin irritation, dermatitis, corrosion of mucous membranes and digestive tract, gastrointestinal tract, kidney damage, and death may be seen in humans due to exposure to this compound (U.S. EPA, 1994c).As chronic effects, kidney damage, increased salivation, inflammation in gums, black lines on the teeth, renal damage, and pink disease in children are the possible diseases (U.S. EPA, 1994).In addition, in terms of its carcinogenic health effects, mercury is classified in Group C (See Appendix A). There is lack of data on human and limited data on animals (rats and mice). In animals, tumors and adenomas in thyroid follicular cell, papillary hyperplasia and squamos cell papillomas, renal adenomas, and tumor have been observed but the studies are inadequate (U.S. EPA IRIS, 2012).

Nickel (Ni): Nickel is a micronutrient which is essential for human body in small amounts. Nickel in sewage sludge is due to food processing, sanitary installations, rechargeable batteries, protective coating, corrosion of equipment of launderettes, jewellery shops, and electroplating shops (EU Commission, 2001).

As other micronutrients, Nickel has adverse effects on human health when exposed at large amounts. Among non-carcinogenic effects, decrease in organ and body weights, neonatal mortality, chronic dermatological (nickel dermatitis, hand eczema), respiratory (asthma, nasal septal perforations, chronic rhinitis and sinusitis, chronic respiratory tract infections), endocrine (hyperglycemia), and cardiovascular effects can be seen due to high level of exposure to nickel. In addition, acute effects are

seen due to the most toxic nickel containing compound nickel carbonyl Ni $(CO)_4$.The effects are chest pain, dry coughing, hyperpnoea, cyanosis, gastrointestinal symptoms, sweating, visual disturbances, and weakness (US EPA, 1986).

For carcinogenic effects, soluble salts of nickel have not been analyzed. Only three compounds, nickel refinery dust, nickel carbonyl and nickel subsulfide are classified as carcinogens. Nickel refinery dust and nickel subsulfide are classified as Group A and nickel carbonyl is classified as Group B2 (See Appendix A) (U.S. EPA IRIS, 2012; U.S. EPA, 1986).

Zinc (Zn): Zinc is an essential trace element for humans. It is an important constituent for enzymes and proteins (Hambridge*et al*., 1987 cited in Epstein, 2003). In addition, it takes part in DNA and RNA synthesis and cell proliferation (U.S. EPA IRIS, 2012). Zinc and its compounds are detected in sewage sludge due to domestic sources such as corrosion and leaching of plumbing, water-proofing products, anti-pest products, wood preservatives, cosmetics and pharmaceuticals and commercial sources such as galvanization processes, alloy production, battery production, building materials, plastics, rubber, fungicides, paper, textiles, and dentistry (EU Commission, 2001).

Insufficient or excessive intake of zinc may result in adverse effects on humans. According to the studies, excessive oral intake of zinc may result in decrease in erythrocyte Cu-Zn-superoxide dismutase (ESOD) activity, copper deficiency, abdominal cramps, vomiting, nausea, and low HDL level (U.S. EPA IRIS, 2012). For inhalation exposure, metal fume fever symptom followed by flu-like symptoms, chills, fever, profuse sweating, headache, and weakness may be seen as acute effects (U.S. EPA, 2005b). For carcinogenicity of zinc exposure, adequate human studies are not available (U.S. EPA 2005b).

2.5.2. Health Effects of Organic Pollutants on Humans

From among the seven trace organic contaminants, the most commonly found and currently analyzable in the laboratory of METU Environmental Engineering Department are also included in the health risk calculations during this study. These chemicals are PCBs and Nonylphenols. Below, a brief discussion of health effects of these chemicals are included.

PCBs: Polychlorinated biphenyl is a group of synthetic organic chemicals. PCBs do not have a natural source in the environment. They were used mainly in transformers, capacitors and electrical equipment due to their good insulation properties in the past. They have many carcinogenic and non-carcinogenic health effects on humans and other living organisms (ATDSR, 2000).

According to studies conducted on humans and animals to determine non-cancer effects of PCBs, it is found that they have toxic effects on the immune system (infection with the Epstein-Barr virus), reproductive system (decrease in birth weight and gestational age), nervous system (learning deficits and changes in activity), and endocrine system (effecting thyroid hormone levels in infants) of humans. In addition, dermal and ocular effects, increase in blood pressure and increase in serum triglyceride and serum cholesterol levels due to increasing levels of PCBs in serum are also seen in humans (U.S. EPA, 2011).

PCBs are classified in Group B2 by U.S. EPA (See Appendix A) due to their carcinogenic effects. Human carcinogenicity data is inadequate but suggestive for carcinogenicity of PCBs. There are studies conducted on workers to determine the carcinogenicity of PCBs. Gastrointestinal tract cancer, hematologic cancer, liver cancer, and gall bladder cancer have been observed in humans during studies. In addition, due to transformation of PCBs into chlorinated dibenzofurans, a highly carcinogenic chemical, cancer incidents can be traced back to PCBs. In Japan and Taiwan, due to consumption of rice oil containing PCBs, liver cancer has been observed since heating up of rice oil results in formation of chlorinated dibenzofurans (U.S. EPA IRIS). Tumor promoting activity is also observed in PCB mixtures and congeners (U.S. EPA, 1996).

Although human data is considered as inadequate, animal data is sufficient for carcinogenicity of PCBs. There are studies on rats showing the incidence of cancer risk. Increasing in incidence of

adenomas and tumors in livers and thyroids has been observed during studies on rats (U.S. EPA IRIS, 2012).

NPEs: NPE is the summation of nonylphenol (NP) and nonylphenolethoxylates with 1 and 2 ethoxy groups. Nonylphenolpolyethoxylates (NPEOs) are one of the two sub-classes of alkylphenolpolyethoxylates (APEs). NPEOs are known to degrade rapidly in nature, which proceeds by the removal of one ethoxy group from the molecule. The final products of degradation are nonlyphenols (NPs). NPEOs are used in many industries such as textile processing, pulp and paper processing, paints, resins, protective coatings, oil and gas recovery, steel manufacturing and power generation. In addition, NPEOs are also used in households as cleaning products, cosmetics and paints. Due to their widespread use they are released into the environment by wastewater treatment plant effluents. They have some health effects on humans and other living organisms (Canada Environmental Protection Act, 2001).

Data on non-carcinogenic effects for humans are very limited. Acute toxicity due to oral and dermal exposure is low. NPs may cause irritation and corrosion (irreversible damage) to skins and eyes on humans but they do not have a high potential for skin sensitization that lead to an allergic response after exposure (U.S. EPA, 2010 & UNECE, 2004). For reproductive and developmental effects, human data are very limited. There is a study on exposed children showing puberty at an early age due to NP exposure (California Environmental Protection Agency, 2009). For NPEOs, some non-carcinogenic effect data are available for humans. Nonylphenol-4-polyetoxylate exposure may cause erythema. Nonylphenol-9-polyetoxylate may cause congenital malformations; however, the weight of evidence is very limited. In addition, other nonylphenolpolyethoxylates (NP6EO, NP10E0 and NP12EO) may cause contact dermatitis and contact photosensitivity (CEPA, 2001).

Apart from acute effects, NP and NPEOs cause estrogenic responses in aquatic organisms and may have reproductive effects (CEPA, 2001). They interfere with estrogenic hormones such as oestradiol, which is an important hormone for female sex characteristics and sex organs (Warhurst, 1995). In addition, alkylphenolethoxylates containing nonylphenols and octylphenols may mimic natural hormones by interaction with the estrogen receptor (Ying *et al*., 2002).

Since the non-carcinogenic data is very limited for humans, the animal data become more important. The effects of NP on animals are more evident. NP is acutely toxic to fish, invertebrates and algae (CEPA, 2001). Excessive salvation, diarrhea, lethargy, erosion of stomach mucosa, skin and eye irritation and irritation of respiratory tract have been observed in laboratory animals (European Chemicals Bureau (2002). As reproductive and developmental effects, decrease in male sex hormone testosterone and increase in uterine weight and hyperactivity may be observed (California Environmental Protection Agency, 2009). In addition, exposure to NP of laboratory animals may cause changes in estrous cycle length, timing of vaginal opening, ovarian weight and sperm count (US EPA, 2010). There is some evidence showing NP have immune effects in animals. In addition, NP may cause nervous system effect such as neurodegeneration (California Environmental Protection Agency, 2009).
The carcinogenic effects of NP on humans are not available. In very low concentrations of NP (as 200 μg/l), human breast cancer cell growth is affected (Warhurst, 1995). On the other hand, genotoxic or non-genotoxicmechanisms causing cancer are considered as low due to NP being unlikely to be mutagenic (European Chemicals Bureau, 2002). The data are limited, so there is no clear evidence whether NP is carcinogenic or not.

2.6. Health Risk Assessment Methodology

Health risk assessment can be defined as the methodology which estimates the impact of environmental pollution on the health of exposed population (World Health Organization, 2004). It includes four main steps (Figure 2.3) (National Research Council, 1983).

In *Hazard Identification*, contaminants that pose a health hazard to humans and their possible health problems are identified (U.S. EPA, 2005a). In *Dose-Response Assessment* potential risks to humans at different exposure levels of interest are evaluated (U.S. EPA, 2005a). In *Exposure Assessment*, magnitude, frequency, duration and route of exposure are identified (U.S. EPA, 1988). Finally, in *Risk*

Characterization, the information from previous steps are put together in order to provide qualitative and quantitative expressions of risk (National Research Council, 1994).

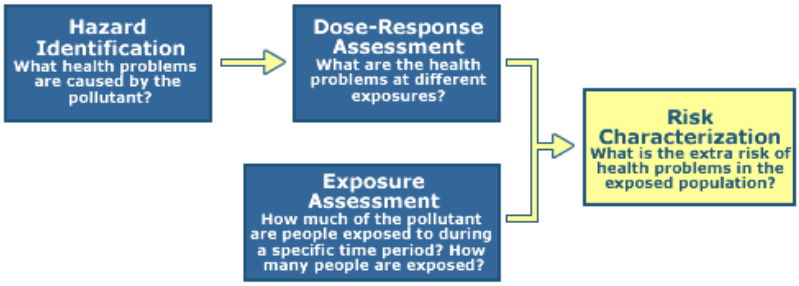

Figure 2.3: Steps of Health Risk Assessment (U.S. EPA, 2013a).

2.6.1. Health Risk Assessment for Land Application of Biosolids in Different Countries

Due to a number of pollutants present in biosolids, health risk-based studies need to be carried out before biosolids are applied to the land to prevent adverse health effects (National Research Council, 2002).Various studies on risk assessment for land application of sewage sludge have been conducted in the world. The oldest and one of the most extensive studies was conducted by U.S. EPA in 1993 (Part 503 Rule).In Part 503 Rule, U.S. EPA's health risk assessment procedure was followed in order to determine risk-based pollutant limits for heavy metals associated with land application of biosolids (U.S. EPA, 1995). Then, these pollutants limits were set into Part 503 Rule.

In France, INERIS (Insitut National de l'Environnement Industriel et des risqué) prepared a document called 'Public Health Risk Assessment of Sludge Land Spreading' in 2008 for European Federation for Agricultural Recycling (EFAR). The study aimed to give a quantitative risk assessment methodology for sludge land spreading by classical risk assessment methods in accordance with the sludge land spreading regulatory considerations. Within the scope of the study, health risks associated with land spreading of sludge were calculated for the pathways related to inhalation and ingestion and the health risks were found to be at acceptable levels for each receptors which are farmers, adults and children (INERIS, 2008).

In Norway, the Norwegian Scientific Committee for Food Safety (VKM) prepared a health risk assessment report named 'Risk Assessment of Contaminants in Sewage Sludge Applied on Norwegian Soils' in 2009 including risks for heavy metals, organic pollutants, and pharmaceuticals due to use of sewage sludge on agricultural land and park areas (VKM, 2009). The health risks were calculated for soil environment, aquatic environment, food producing animals and humans (adults and children). According to the results of the study, all risks to the receptors given above were considered to be low.

Apart from these studies, there are further studies related to ecological and health risk assessment associated with land application of biosolids for organic pollutants such as linear alkyl benzene sulfonate (LAS) (Schowanek *et al.*,2007; Wolf and Feilfel, 1998), polybrominated diphenyl ethers (PBDEs) (Yang *et al.*,2007; Cincinelli *et al.*,2012), nonylphenol and nonylphenolethoxylates (Gonzalez *et al.*, 2009) and persistent organic pollutants (POPs) (Passuello *et al.*, 2010).

In Turkey, there are some studies related to health risk assessment associated with inorganic and organic pollutants. Health risk assessment of trace elements on ingestion of soil (Guney *et al.*, 2010), exposure and risk assessment of black tea in terms of trace elements (Sofuoglu and Kavcar, 2008) and exposure and risk assessment for ingestion of drinking water (Kavcar *et al.*, 2009) are some of the studies conducted in Turkey. However, no studies related to health risk assessment for land application of biosolids have been found. This study aims to fill in the gap on health risk assessment for land application of biosolids in Turkey and to determine health risks associated with land application of biosolids originating from a metropolitan city. In the following sections, the two different approaches (U.S. EPA and INERIS) used in this study are explained in detail.

2.6.1.1. U.S. EPA Health Risk Assessment Procedure for Land Application of Biosolids

U.S. EPA's health risk assessment procedure for biosolids includes four main steps (U.S. EPA, 1995) as explained above. Each one of these steps in land application of biosolids context is explained in detail in the following sections.

Hazard Identification

Identification of pollutants is an important step of the risk assessment procedure. Intra-Agency Biosolids Task Force listed 200 pollutants for review in 1984 considering the available data on human exposure and health effects, effects on animals including domestic animals, wildlife and plants, phototoxicity, plant uptake and pollutant occurrence frequency in the biosolids. After listing 200 pollutants, they were eliminated according to the probability of toxicity, the likelihood of human and environmental exposure, exposure data and professional judgment. After elimination, 50 pollutants were chosen to be reviewed further (U.S. EPA, 1995).

After reviewing 50 pollutants for further consideration, the ratios of estimated concentrations of pollutants in environment (soil, plant or animal tissue, water or air) to lowest concentrations of pollutants toxic to organism for each pollutant were calculated (U.S. EPA, 1995). The ratios with values less than 1 were eliminated and remaining pollutants were ranked through a ranking process in order to determine a priority list. Finally, 24 pollutants were chosen for land application of biosolids (Table 2.5) (U.S. EPA, 1995).

Table 2.5: Chosen Pollutants for Land Application after Hazard Characterization (U.S. EPA, 1995)

Organics	**Inorganics**
Aldrin/dieldrin	Arsenic
Benzene	Chromium
Benzo(a)pyrene	Cadmium
Bis2(ethylhexyl) phthalate	Chromium
Chlordane	Copper
DDT/DDE/DDD	Mercury
Heptachlor	Molybdenum
Hexachlorobenzene	Nickel
Hexachlorobutadiene	Selenium
Lindane	Zinc
N-Nitroso-dimethylamine	
PCBs	
Toxaphene	
Trichloroethylene	

The Rule is reviewed biennially and inclusion of various pollutants found in biosolids is evaluated through assessing available data on pollutants to determine whether exposure and hazard screening assessment can be conducted or not. If data are available for pollutants, the human health and ecological hazard screening assessment are conducted and potential risks are determined. Three biennial reviews (in 2003, 2005 and 2007) have been conducted until now and no new pollutants have been added to the rule.

Exposure Assessment

Exposure assessments were conducted for all three disposal methods: land application, monofilling and incineration. In this study, only exposure assessment for land application of biosolids is discussed. The following receptors and pathways are considered for land application of biosolids.

Receptors:

Both human (child, home gardener) and ecological receptors (soil organisms, animals, and plants) were considered for risk assessment studies of land application. In human health risk assessment of land application of biosolids, highly exposed individual (HEI) was used as the receptor. HEI is defined by U.S. EPA as "an individual who remains for an extended period of time at or adjacent to the site where the maximum exposure occurs" (U.S. EPA, 1995).

Pathways:

An exposure pathway can be identified as a individual mechanism by which a population may be exposed to the pollutants (U.S. EPA, 1988). In Part 503 Rule, a total of 14 pathways were considered. Each one of these pathways and associated receptors are summarized in Table 2.6.

Table 2.6: Summary of Exposure Pathways and Receptors Selected by U.S. EPA (U.S. EPA, 1995)

Pathway	**Receptor**
1.Biosolids→Soil→Plant→Human	Human (except home gardener) lifetime ingestion of plants grown in biosolids-amended soil
2. Biosolids →Soil →Plant →Human	Human (home gardener) lifetime ingestion of plants grown in biosolids-amended soil
3. Biosolids →Human	Human (child) ingestion biosolids
4. Biosolids →Soil →Plant →Animal →Human	Human lifetime ingestion of animal products (animals raised on forage grown on biosolids-amended soil)
5. Biosolids →Soil→ Animal →Human	Human lifetime ingestion of animal products (animals ingest biosolids directly)
6. Biosolids →Soil →Plant →Animal	Animals lifetime ingestion of plants grown on biosolids-amended soil)
7. Biosolids →Soil→ Animal	Animals lifetime ingestion biosolids
8. Biosolids →Soil →Plant	Plant toxicity due to taking up biosolids pollutants when grown in biosolids- amended soils
9. Biosolids →Soil → Soil →Organism	Soil organism ingesting biosolids/ soil mixture
10. Biosolids →Soil → Soil → Organism →Soil → Organism → Predator	Predator of soil organism that have been exposed to biosolids-amended soil
11. Biosolids →Soil →Airborne Dust →Human	Adult human lifetime inhalation of particles (tractor driver tilling a field)
12. Biosolids →Soil →Surface Water →Human	Human lifetime drinking water and ingesting fish containing pollutants in biosolids
13. Biosolids →Soil →Air →Human	Human lifetime inhalation of pollutants in biosolids that volatilized to air
14. Biosolids →Soil→ Groundwater→ Human	Human lifetime drinking well water containing pollutants from biosolids

Dose-Response Evaluations

In this step, U.S. EPA used reference doses (RfD) and cancer potency factors (q_1^*) in order to determine toxic effects of pollutants on humans. q_1^* s are used to evaluate human cancer risks when the receptor is exposed to a pollutant during 70 years lifetime. Cancer potency factors can be determined using most sensitive animals in laboratory experiments and conservative extrapolation of data from high doses of animals used in laboratory experiments to low dose of human exposure. RfD can be defined as the daily oral exposure dose to the human population that is likely to be without an appreciable risk of adverse effects during a lifetime and used for non-cancer risk assessments (U.S. EPA, 2013b). Both RfD and q_1^* values for pollutants selected in the study are available in U.S. EPA IRIS database.

Risk Characterization

In risk characterization, first, risk-based pollutant limits were defined for each pathway and each pollutant by U.S. EPA. Pollutant limits were named as RSC (Reference Pollutant Concentration in Biosolids) or RP_c (Reference Cumulative Application Rate of Pollutant). RSC is defined as 'the pollutant concentration in biosolids that can be ingested without adverse effects'. RP_c is defined as "the cumulative amount of pollutant that can be applied to a hectare of land without adverse effects" (Table 2.7). RSC and RP_c values were calculated for each pathway for land application of biosolids.

Table 2.7: Risk Assessment Results for All Pollutants and Pathways (U.S. EPA, 1995)

Pathway No	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pollutant	**RP_c**	**RP_c**	**RSC**	**RP_c**	**RSC**	**RP_c**	**RSC**	**RP_c**	**RP_c**	**RP_c**	**RP_c**	**RP_c**	**RP_c**	**RP_c**
Arsenic	6700	930	41	-	-	1600	3100	-	-	-	-	66000	-	1200
Cadmium	610	120	39	1600	68000	140	650	-	-	53	-	63000	-	unlimited
Chromium	-	-	79000	-	-	-	190000	3000	-	-	-	unlimited	-	12000
Copper	-	-	10000	-	-	3700	2000	1500	2900	-	-	unlimited	-	unlimited
Lead	-	-	300	-	-	11000	1200	-	-	5000	-	unlimited	-	unlimited
Mercury	180	370	17	1500	24000	-	-	-	-	-	-	1100	-	unlimited
Molybdenum	-	-	400	-	-	18	530	-	-	-	-	-	-	-
Nickel	63000	10000	820	-	-	1800	5400	420	-	-	-	unlimited	-	13000
Selenium	14000	1200	100	15000	13000	790	130	-	-	-	-	-	-	-
Zinc	16000	3600	16000	150000	220000	12000	36000	2800	-	-	-	-	-	-

RP_c: Reference cumulative application rate of pollutant for inorganic pollutants and non-degraded organic pollutants (kg-pollutant/hectare)
RSC: Reference pollutant concentration in biosolids (µg-pollutant/g-biosolids DW)
-: Not calculated (excluded during the hazard assessment or lack of data)
Unlimited: No application rate resulted in adverse effects

After calculation of RSC and RP values for each pathway, the lowest risk-based pollutant limits were selected comparing the results of all pathways for pollutants. Risk-based pollutant limits and most limiting pathways values are presented in Table 2.8.The pollutant limit values are both given as RP_c and RSC. RP_c values can be converted into RSC values assuming that application rate is 10 tons biosolids /year.ha and land application lasts for 100 years (U.S. EPA, 1995)

Table 2.8: Pollutant Limits and Limiting Pathways for Biosolids Identified in Land Application (U.S. EPA, 1995)

Pollutant	**Limiting Pathway**	**Pollutant Limit (as RP_c) (kg-poll./ha)**	**Pollutant Limit (as RSC) (µg-poll./g-biosolids DW)**
Arsenic	Child Eating Biosolids (3)	41	41
Cadmium	Child Eating Biosolids (3)	39	39
Chromium	Plant Phytotoxicity (8)	3000	3000
Copper	Plant Phytotoxicity (8)	1500	1500
Lead	Child Eating Biosolids (3)	300	300
Mercury	Child Eating Biosolids (3)	17	17
Molybdenum	Animal Eating Feed (6)	18	18
Nickel	Plant Phytotoxicity (8)	420	420
Selenium	Child Eating Biosolids (3)	100	100
Zinc	Plant Phytotoxicity (8)	2800	2800
PCBs	Adult Eating Animal Products (animal ate biosolids) (5)	4.6	4.6

In Part 503 Rule, four different types of pollutant limits are given (Table 2.9). Cumulative Pollutant Loading Rates (CPLRs) are pollutant limits calculated in risk assessment study for biosolids land application. These pollutant limits are only applied to biosolids applied in bulk. Annual Pollutant Loading Rate (APLR) values are derived from CPLR values. These values can be found dividing CPLR values by 20 assuming that 20 applications are done at the same rate to a site. APLR limit values are applied to biosolids that are sold or given away in bags or other containers. Finally, Ceiling Concentration Limit indicates maximum allowable concentration that can be applied to lands. These concentration limits were taken from National Sludge Survey (NSSS) which was conducted by U.S. EPA in 1990 to identify the type of pollutants present in sludge (U.S. EPA, 1995). Ceiling Concentration limits were put into the Part 503 Rule in order to prevent biosolids having high metal concentrations. Finally, pollutant concentrations limits were directly taken from risk assessment results as stated above (U.S. EPA, 1995).

According to the Part 503 Rule, bulk biosolids or biosolids sold or given away in a bag or container cannot be applied to land if one of the ceiling concentration limits has been exceeded. Bulk biosolids cannot be applied to agricultural land, forest, a public contact site, or a reclamation site if any of the CPLR limits has been exceed or any of the pollutant concentration limits has been exceeded. In addition, it cannot be applied to a lawn or a home garden, if any of the pollutant concentration limits has been exceeded. On the other hand, biosolids sold or given away in a bag or container cannot be applied to land if any of the APLR limits has been reached or any of the pollutant concentrations has been exceeded.

Table 2.9: The Part 503 Rule Concentration Limits (U.S. EPA, 1995)

	CPLR Limit (kg poll./ha, DW)	APLR Limit (kg poll./ha/year, DW)	Ceiling Concentration Limit (mg-poll./kg biosolids, DW)	Pollutant Concentration Limit (mg-poll./kg biosolids, DW)
Arsenic	41	2	75	41
Cadmium	39	2	85	39
Chromium	-	-	-	-
Copper	1500	75	4300	1500
Lead	300	15	840	300
Mercury	17	0.85	57	17
Molybdenum	18		75	
Nickel	420	21	420	420
Selenium	100	5	100	100
Zinc	2800	140	7500	2800

The risk assessment for organics were evaluated but not included in Part 503 Rule document since their use were banned or restricted in United States (U.S. EPA, 1995). In addition, the concentration of organics in biosolids were very low and the limits of these pollutants were not likely to be exceeded when applied to land, incinerated or removed as surface disposal (U.S. EPA, 1995).

Equations Used in Risk Characterization

In U.S EPA's approach, as stated before, 14 pathways were evaluated. For each pathway, different equations were used to determine pollutant limit concentrations (U.S. EPA, 1995).In this study, only Pathway 3 (child ingestion biosolids) was used due to being one of the most limiting pathways in U.S. EPA's method (U.S. EPA, 1995). In addition, the other pathways were not assessed due to lack of site-specific data (See Section 3.2.1.2 for discussion in detail). The reason for this is only the equations of Pathway 3 for both cancer and non-cancer risks are given in detail.

Non-Cancer Risk Equations for Child Ingesting Biosolids Pathway

Non-cancer health effects were evaluated through a Hazard Index (*HI*) value (U.S. EPA, 1995).In the study of U.S. EPA, '*HI*' term was used in order to define 'the ratio of the potential exposure to the substance and the level at which no adverse effects are expected' (U.S. EPA, 2013c). *HI* can be determined using the following equation (U.S. EPA, 1995):

$$HI_i = \frac{C_i * Is * DE * RE}{RfD_i * 10^3 * BW} \quad (2.1)$$

HI_i: Hazard Index of pollutant i
C_i: Concentration of the pollutant$i$ in biosolids (mg pollutant/kg biosolids)
Is: Ingestion rate of biosolids by a child (g biosolids/day)
RfD: Oral Reference Dose of pollutant i(mg pollutant /kg BW.day)
BW: Body weight of a child (kg)
DE: Exposure duration adjustment (unitless)
RE: Relative effectiveness of ingestion exposure (unitless)
10^3: Unit conversion factor (g/kg)

In the Equation 2.1, for body weight (BW) of a child, 16 kg was taken (U.S: EPA, 1995). Moreover, ingestion rate of biosolids was taken as 0.2 g/day (U.S. EPA, 1992). Relative effectiveness (*RE*) is the differences of toxicological effects of pollutants due to route of exposure such as ingestion or inhalation. However, it was taken as 1 since there is limited information for deriving the value (U.S.

EPA, 1992). In addition, for Exposure Duration Adjustment(DE), there was no EPA-approved method to adjust exposure duration with respect to RfDs (based on lifetime exposure). So, it was set to 1 in EPA Part 503 Rule (U.S. EPA, 1992).

Cancer Risk Equations for Child Ingesting Biosolids Pathway

Cancer health effects were evaluated through a $Risk$ value and calculated by the following equation (U.S. EPA, 1995):

$$Risk_i = \frac{C_i * Is * DE * RE * q^*_{1_i}}{BW * 10^3} \quad (2.2)$$

$Risk_i$: Cancer Risk of pollutant i
Ci: Concentration of the pollutant i in biosolids (mg pollutant/kg biosolids)
Is: Ingestion rate of biosolids by a child (g biosolids/day)
q_1^*: Cancer potency factor of pollutant i (mg pollutant /kg BW.day)$^{-1}$
DE: Exposure duration adjustment (unitless)
RE: Relative effectiveness of ingestion exposure (unitless)
BW: Body weight of child (kg)
10^3: Unit conversion factor (g/kg)

In the formula for cancer risk calculation, for body weight (BW) of a child, 16 kg was taken and ingestion rate of biosolids was taken as 0.2 g/kg.day (U.S. EPA, 1992). RE value was set to 1 due to the same reason with HI formula. For DE, 5 years of exposure in life-time span (70 years) was taken and set as 0.0714 (5 years/70 years).

Risk levels are suggested by U.S. EPA between 10^{-4} and 10^{-6} in establishing various regulations (National Research Council, 2002). For land application of biosolids, risk level was suggested by U.S. EPA as 10^{-4} (U.S. EPA, 1995). It means that there is a 1 in 1000 chance of highly exposed individual getting cancer (U.S. EPA, 1995).

2.6.1.2. INERIS Public Health Risk Assessment Study of Sludge Land Spreading

INERIS conducted a public health risk assessment study in 2008 aiming to evaluate health risks for sludge land spreading according to regulatory aspects. In the study, pollutants and suggested limit values for sludge provided in Proposal for a Directive of the European Parliament of the Council on Spreading Sludge on Land (CEC, 2003) were taken into consideration for the assessment. By this way, pollutants and suggested limit values were evaluated in terms of their relevance with health concerns due to sludge land spreading (INERIS, 2008)

In the study, public health risk assessment was evaluated for both threshold (non-cancer) and non-threshold (cancer) effects. Threshold effects were defined by INERIS as 'the effects for which a threshold of action exists and for which it is possible to find a range of dose without effect'. It corresponds to the non-cancer effects in U.S. EPA's method. On the other hand, non-threshold effects were defined by INERIS as 'the effects for which none threshold of action exists and for each dose, probability of risk exists'. It corresponds to cancer effects in U.S. EPA's method.

During health risk assessment, four steps (i.e., substance selection, toxicity evaluation, exposure evaluation and risk assessment) were followed by INERIS in conducting risk calculations (INERIS, 2008). These steps are analyzed in detail in the following sections.

Substance Selection

In substance selection, the pollutants were chosen from CEC (2003) as stated above. The selected pollutants are given in Table 2.10 (INERIS, 2008).

Table 2.10: Pollutants Evaluated by INERIS (INERIS, 2008)

Organics	Inorganics
PAH	Cadmium
Benzo(a)pyrene	Chromium
PCBs	Copper
PCDD/PCDF	Mercury
NPE	Nickel
LAS	Lead
	Zinc

Toxicity Evaluation

In this step, INERIS identified Toxicological Reference Values (TRVs) for both threshold (non-cancer) and non-threshold (cancer) effects. 'TRV' is both used for threshold and non–threshold effects, however; they do not have the same values. TRV values for threshold effects are used to determine the threshold effects of a pollutant and can be considered as RfD values used in U.S. EPA's method. On the other hand, TRV values for non-threshold effects are used to evaluate human cancer risks and can be considered as q_1^* values used in U.S. EPA's method.INERIS identified TRV values for both threshold and non-threshold effects for ingestion and inhalation pathways and used them for the calculation of health risks (INERIS, 2008). For dermal pathway, no TRV values were suggested due to lack of toxicological data and risk calculations were not calculated for this pathway.

Exposure Evaluation

In exposure evaluation, the possible receptors, pathways and the substance concentration in sludge were discussed by INERIS. In addition, exposure parameters and exposure equations were defined in order to calculate risks for each pathway and receptor (INERIS, 2008). Detailed information is given in the following sections.

Receptor and Pathway Determination

Receptors and pathways identified by INERIS are given in Table 2.11.

Table 2.11: The Selected Pathways and Receptors by INERIS (INERIS, 2008)

Pathway	Receptor
Soil → human (ingestion)	Neighbors, Farmers
Soil → human (inhalation)	Neighbors, Farmers
Soil → human (dermal contact)	Neighbors, Farmers
Soil → terrestrial animals → human(ingestion)	Consumers, Neighbors, Farmers
Soil → vegetables → human(ingestion)	Consumers, Neighbors, Farmers
Soil→ vegetables → terrestrial animals→ human(ingestion)	Consumers, Neighbors, Farmers
Soil→ water(ground/surface) → terrestrial animals → human(ingestion)	Consumers, Neighbors, Farmers
Soil→ water(ground/surface)→ vegetables → human(ingestion)	Consumers, Neighbors, Farmers
Soil→ water(ground/surface) → vegetables → terrestrial animals → human (ingestion)	Consumers, Neighbors, Farmers
Soil → water (ground/surface) →fish→ human (ingestion)	Consumers, Neighbors, Farmers
Soil→ water (ground/surface) → human (ingestion)	Consumers, Neighbors, Farmers
Soil→ water(ground/surface) → human(dermal contact)	Consumers, Neighbors, Farmers

Substance Concentrations

Substance concentration is defined as the concentration of pollutant in soil which is mixed with sludge after consecutive applications of sludge on land. Substance concentrations were used by INERIS in order to calculate associated health risks due to land spreading of sludge. To determine substance concentrations, both background soil concentrations of pollutants and pollutant concentrations in sludge were taken into account. As pollutant concentrations in sludge, the suggested limit values were taken from CEC (2003). Furthermore, background soil concentrations were taken from database of European Federation for Agricultural Recycling (EFAR) and literature. Both soil and sludge concentrations were assumed to be constant over time (INERIS, 2008).

According to INERIS, during land spreading of sludge, sludge is mixed with soil with a dilution factor (DF). DF depends on the application rate of sludge, depth of the soil, and bulk density of the soil (INERIS, 2008). It can be calculated by the equation below (INERIS, 2008):

$$DF = \frac{Application\ Rate}{Soil\ Depth * Soil\ Bulk\ Density} \quad (2.3)$$

An application rate of 3 tons/ ha.yr, a soil depth of 25 cm, and a soil bulk density of 1.3 tons/m^3 were assumed by INERIS (INERIS, 2008). Using DF, diluted pollutant concentrations in sludge were determined after 1 year of application. For cumulative applications, the diluted pollutant concentrations were multiplied by total years of application to determine cumulative inputs due to sludge land spreading. In the study of INERIS, 70 years of application was assumed to occur and the concentrations reach the maximum level after 70 years of application (INERIS, 2008).

For some organic compounds such as NPEs, degradation rates were taken into consideration as well (INERIS, 2008). Substance concentration in year n due to degradation can be calculated by the following formula:

$$Xn = X_1 * e^{(-\ln(2)*(n-1)/\text{half-life})} \quad (2.4)$$

X_n: Substance concentration in year n (mg/kg)
X_1: Substance concentration in 1st year (mg/kg)

For NPE, half-life was assumed to be 0.41 years. For PCBs and heavy metals, it was assumed that degradation did not take place (INERIS, 2008).

After calculation of cumulative pollutant concentrations in sludge applied to soil considered DF and degradation, substance concentration were calculated by the equation below:

$$Substance\ Conc. = Cumulative\ \ Conc. of\ Sludge + Background\ Soil\ Conc. \quad (2.5)$$

Exposure Equation for Child Ingesting Soil Pathway

For each pathway, different exposure equations were used and Daily Exposure Dose (DED) values were determined. DEDcan be defined as the daily dose of a pollutant which is exposed by a receptor. Within the scope of this study, the exposure equation for only ingestion of soil by a child pathway was considered (See Section 3.2.1.2). $DED$for the selected pathway can be calculated by the following equation (INERIS, 2008):

$$DED = \frac{M_{ingestedsoil} * C_i * F}{BW} \quad (2.6)$$

DED: Daily exposure dose (mg/kg.day)
$M_{soil\ ingested}$: Mass of soil ingestion (mg/day)
C_i: Concentration of substance i (mg substance/kg soil)
F: Exposure frequency
BW: Body weight of child (kg)

In this equation, mass of soil ingestion was taken as 150 mg/day for child (INERIS, 2008). Substance concentration (Ci) were determined using cumulative sludge concentrations and background soil concentrations as stated above. Exposure frequency (F) was determined as 0.021 (INERIS, 2008). This value was derived from an assumption stating that daily time exposure outside as 2 hours /day and exposure day per year outside as 92 day/year for child.

Risk Assessment

Risk calculations were carried out by INERIS for both threshold effects and non-threshold effects using TRVs and DED values. In the following sections, equations used in risk calculations by INERIS are given in detail.

Risk Calculation for Threshold Effects

Threshold effects were calculated through a hazard index (HI) value by the equation below (INERIS, 2008):

$$HI = \frac{Daily\ Exposure\ Dose\ (DED)}{TRV_{for\ threshold\ effects}} \tag{2.7}$$

After calculating HI for each pollutant, they were classified according to their target organs and effects of pollutants and summed up according to classification to determine cumulative HI($\sum HI$) for each receptor.Then, $\sum HI$ was compared with '1'In this study, there was no available information to conclude the target organs or effects of pollutants. Therefore, all HI values were summed up due to lack of information and compared with '1'. Summing up all HI values resulted in a conservative approach which was accepted within the scope of the study.

If $\sum HI$ is less than one, it means adverse effects are not considered to be significant, however, if it is more than one, it is likely that the pollutant affects receptor adversely (INERIS, 2008).

Risk Calculation for Non-Threshold Effects

Risk calculation for non-threshold effects was based on excess of risk (ER). It was calculated using the following equation (INERIS, 2008):

$$ER = Daily\ Exposure\ Dose\ (DED) * TRV_{\ for\ non-threshold\ effects} \tag{2.8}$$

To determine cumulative ER value ($\sum ER$), ER values of each pollutant which have non-threshold effects were summed up and $\sum ER$ for each receptor was found (INERIS, 2008).For non-threshold effects the acceptable risk levelwas taken as 10^{-5} (INERIS, 2008) which is smaller than the value used in U.S. EPA approach (10^{-4}) (U.S. EPA, 1992).

The results of the INERIS's study stated that the main contribution to the risk was coming from ingestion of plants and animal products. In addition, background pollutant concentrations in soil and food have more contribution when compared to pollutant concentrations in sludge limit values (from

CEC, 2003). However, the risks due to threshold and non-threshold effects were considered as acceptable for each receptor (INERIS, 2008).

2.6.1.3. Comparison of U.S EPA and INERIS's Methods

U.S. EPA and INERIS conducted health risk calculations for different purposes. U.S. EPA aimed to determine risk-based pollutant limits to be put in Part 503 Rule. Health risks of pollutants were calculated for each pathway and each pollutant and the lowest pollutant limits for each pollutant were selected as the risk-based pollutant limits. On the other hand, INERIS aimed to calculate health risks for the suggested limit values provided in CEC (2003) and to evaluated these limit values in terms of relevance with health concerns due to sludge land spreading. For Threshold (non-cancer) risks were summed up for each receptor (in terms of chemicals and pathways) and a cumulative threshold risk was determined. In addition, same calculations were also conducted for non-threshold (cancer) risks.

Apart from differences in the purposes and methods of the studies, health risk calculations for exposure pathways have also some differences. Health risk calculations for ingestion by a child pathway which is the concern of this study differ for both methods. In U.S. EPA's method, biosolids which is undiluted is ingested by a child and pollutant concentrations in biosolids were taken into account for health risk calculations. Conversely, in INERIS's method, soil which is mixed with sludge is ingested by a child. For the calculation of health risks, substance concentrations which are the summation of background soil concentration of pollutant and cumulative pollutant concentrations in sludge were considered. For the calculation of cumulative sludge concentrations, dilution factor of sludge, degradation of pollutants and total years of application were taken into account. In addition, as another difference, for the calculation of health risks, in INERIS's method, an exposure frequency was assumed. Such an assumption was not included in the U.S. EPA's method and DE was set to 1.

CHAPTER 3

MATERIALS AND METHODS

This part includes both experimental work and health risk assessment methodology followed in this study.

3.1. Analytical Work

In this section, the area of the study, sampling, pretreatment and analysis of sludge are discussed in detail.

3.1.1. Area of the Study

Sludge samples were taken from Ankara Central Wastewater Treatment Plant. Monthly samples were collected from January, 2012 to December, 2012 in order to observe monthly variations in heavy metal and organic contaminant concentrations in sludge and time dependent variations in health risks.

Ankara Central Wastewater Treatment Plant was constructed and set into operation in 1997 with a design capacity of 765,000 m^3 wastewater daily. It has main processes for wastewater treatment such as preliminary treatment including screening and grit chambers, primary sedimentation tank, aeration tank and secondary sedimentation tank (Figure 3.1). For sludge treatment, raw sludge (sludge from primary sedimentation tank and waste activated sludge from secondary sedimentation tank) is thickened in gravity thickener first, and then transferred to anaerobic stabilization tank. After then, digested sludge is carried to the gravity thickener and finally, it is dewatered by decanter centrifuge system (ASKİ, 2012).

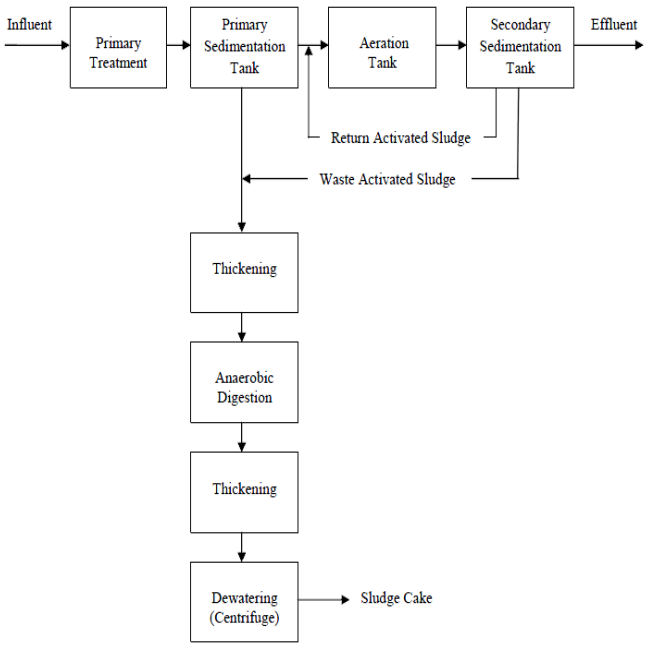

Figure 3.1: Flowchart of ACWWTP

3.1.2. Sampling of Sludge

Dewatered sludge samples were taken directly from the outlet of the centrifuge decanter system and were carried to the laboratory in a cooler. Samples were put into freeze-dryer in order to achieve dried and homogenized samples. After drying, the samples were sieved with 1.7 mm-size sieve and stored in amber-glass bottles.

3.1.3. Pretreatment and Analysis of Sludge

Before analysis of pollutants in sludge, some pretreatment processes should be done. Heavy metals in sewage sludge cannot be analyzed by atomic adsorption spectrometry without acid digestion since digestion transforms metals to free metal form which can be detected by atomic adsorption spectrometry. In addition, digestion also helps to prevent interferences due to organic matter in samples (APHA, AWWA, WEF, 2005).

PCBs and NPEs, on the other hand, should be removed from sludge solids by extraction methods in order to be able to analyze their concentrations. In the following sections, pretreatment and analysis methods for heavy metals, PCBs and NPEs are discussed in detail.

3.1.3.1. Total Solids Determination

For solids analysis, Method 2540 B (APHA, AWWA, WEF, 2005) was followed and the results are given in Table 3.1. Total solids are required to convert concentration units to mg/kg dry weight.

Table 3.1: Total Solids (%) of Dried Sludge Samples

Sampling Month (2012)	Total Solids (TS%)
January	96.7
February	93.4
March	92.7
April	93.8
May	93.8
June	92.2
July	94.1
August	96.0
September	91.8
October	90.1
November	92.3
December	93.0

3.1.3.2. Acid Digestion and Atomic Absorption Analysis Procedure for Heavy Metals

For digestion of metals, nitric acid (HNO_3) is usually chosen for easily oxidized samples. Since sewage sludge samples are difficult to be oxidized in terms of organic matter, perchloric acid ($HClO_4$) addition to HNO_3 was selected to be used in the study as the digestion procedure (Method 3030 H) (APHA, AWWA, WEF, 2005).

For the digestion step (Method 3030H), initially, triplicate samples of 0.5 g dried sludge was weighted and put into a teflon beaker. Then, 10 mL of HNO_3 was added to the teflon beaker and it was closed by a teflon cap. After adding 10 mL of HNO_3, the teflon beaker was placed on the hot plate, evaporated for 1 hour until the sample did not boil and then, the teflon beaker was cooled down. 10 mL of HNO_3 was added again and evaporated for 1 hour. Then, after cooling the beaker, 5 mL $HClO_4$ was added to the beaker and evaporated until white fumes of $HClO_4$ appeared. After evaporation

process, the sample was cooled down and filtered by using coarse filter paper. Then, the digested sample was poured into the 50 mL volumetric flask. Finally, sample was diluted to 50 mL with ultra-pure water and mixed thoroughly. A flow chart of the digestion procedure is given in Figure 3.2.

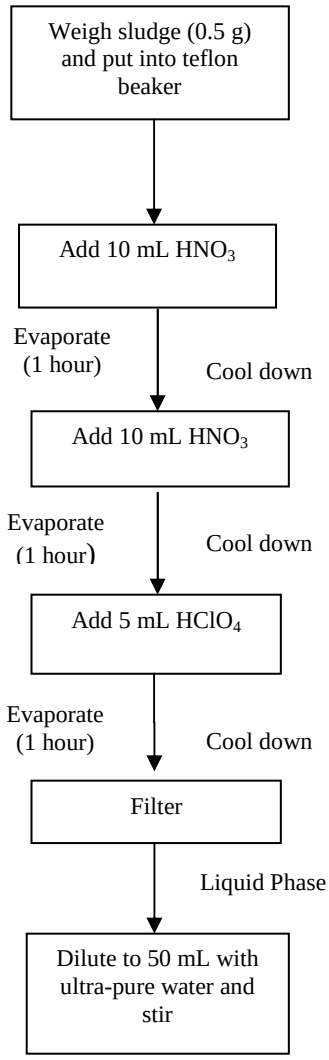

Figure 3.2: Flowchart for Nitric Acid -Perchloric Acid Digestion Procedure

After digestion, the samples became ready for heavy metal analysis. In this study, for heavy metal analysis except for Hg and Cd, flame atomic absorption spectrometer (Perkin Elmer 400-AA Analyst) was used. For Hg, an additional system (MHS-15) was attached to the Perkin Elmer 400-AA Analyst. For Cd analysis, a graphite furnace system (HGA 900) was attached to the Perkin Elmer 400-AA Analyst to determine Cd concentrations in sludge samples.

The working principle of atomic adsorption spectrometer is based on absorption of light due to atomized element (Figure 3.3).First, test solution is aspirated by nebulizer to flame. Then, atomic light beam coming from hallow cathode lamp is passed across the flame and goes to a monochromator. Finally, sample is transferred to a detector which determines the amount of light absorption by atomized element included in the flame and absorption data is analyzed in data processor for determination of concentration of the atomized element (APHA, AWWA, WEF, 2005).

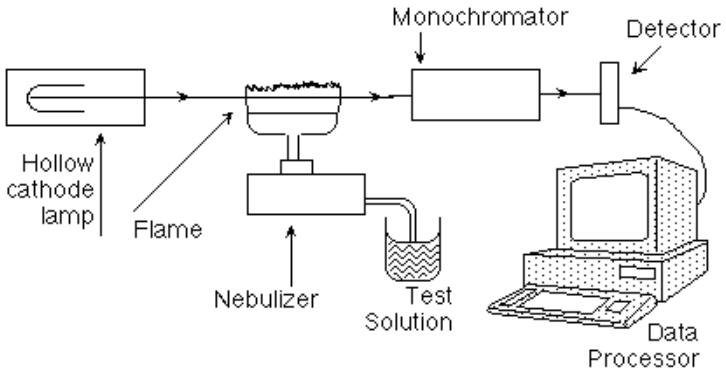

Figure 3.3: Schematic view of AAS (New Mexico State University, 2012)

In this study, for the analysis of five heavy metals (Cr, Cu, Ni, Pb, Zn), first, air and acetylene valves were opened and a hollow-cathode lamp (specific for each heavy metal) was set, and current and wavelength were arranged according to the heavy metal to be analyzed. It took 15-20 minutes for hallow cathode lamp to warm up and energy source to be balanced. After, the flame was ignited, and the system was waited for stabilization. At first, 1L of blank sample (2% HNO_3 v/v) and calibration standards using High Purity Standards, QCS-27 were prepared. Calibration standards were prepared for 0.1 ppm, 0.3 ppm, 0.5 ppm, 1 ppm, 2 ppm, 3 ppm, and 4 ppm. For each heavy metal to be analyzed, three calibration standards were used according to recommended conditions provided in software system of the analyzer.After blank and calibration preparation, blank sample was aspirated to the nebulizer and analyzed. Calibration standards were also aspirated and calibration curve was obtained. Correlations for calibration curve were observed between 0.999 and 0.995. After calibration was done, triplicate samples were analyzed and for each sample AAS processed triplicate concentrations. By this way, for each sample, nine concentration values were measured. Between two samples, blank sample was aspirated to clean nebulizer. After operation, analyzer and flame was put off, remaining gas was ejected, and acetylene and air flows were turned off (Method 3111B) (APHA, AWWA, WEF, 2005).

Hg concentrations in sludge samples were analyzed with cold-vapor technique since Hg concentrations could not be detected with AAS itself. MHS-15 Mercury/Hydride System was attached to Perkin Elmer 400-AA Analyst to be able to determine Hg concentrations in digested samples. The system includes a reaction system and quartz cell system (Perkin Elmer, 2012). The reaction system includes two flasks. One of them includes $NaBH_4$ (3% w/v) which is used as the reducing agent. The other one is for samples. As $NaBH_4$ is transferred to the sample flask with a connected pipe, mercury is reduced in its metallic state. After then, mercury in metallic state is carried by argon gas to the quartz cell for analysis (Method 3112 B) (APHA, AWWA, WEF, 2005).

In the analysis, first, blank (1.5 % HCl v/v) and calibration standards (High Purity Standards, 100 33-1, 100 µg/mL Mercury in 5%) were prepared. Calibration standards were prepared for 5 ppb, 10 ppb and 20 ppb. Then, AAS was turned on and source lamp was opened to warm up. At this time, argon gas and air was turned on. After warm up, 10 mL of blank sample was placed to the MHS-15 system. Additionally, $NaBH_4$ was also placed to the system. $NaBH_4$ was injected to the blank sample for 5 seconds and waited for analysis of the blank sample. After that, three calibration standards (10 mL) were analyzed with same procedure and the calibration curve with a correlation of 0.985 was obtained. Finally, triplicate samples (10mL) were analyzed with the same procedure. Just before analysis of samples and calibration standards, one drop of $KMnO_4$ (5% w/v) was added to the samples for stabilization. After operation, analyzer, argon and air flows were turned off.

Cd concentrations in sludge samples were also analyzed with a different technique which is HGA 900 Graphite. HGA is used for electrothermal atomization of pollutants which are below the detection ranges of AAS. The main units of HGA system are a graphite furnace with a power unit and AS-800 auto-sampler (Perkin Elmer, 2003). The working principle is the similar with flame atomic absorption. Only one difference is the use of graphite furnace for atomization rather than burner system included in flame atomic absorption. In graphite furnace, the samples are heated more than one stage. In the

first stage, graphite tube is heated and sample is dried at about 120 ˚C. In the second stage, organic matter and other matrix components are destroyed with a higher temperature (850˚C) and in the third stage; atomization for the element to be determined occurs at 1650˚C. In the final step, the tube is cleaned at 2400˚C to be ready for next analysis (Perkin Elmer, 2003; APHA, AWWA, WEF, 2005).

For the analysis, first, the AAS system, HGA system and cooling system were turned on. In addition, the flow of argon gas was also turned on. Source lamp of Cd was selected for the analysis and waited for warm-up. The auto sampler was aligned before analysis in order to prevent sticking of auto sampler arm to the graphite tube or auto sampler tray. After, the calibration standard was prepared with High Purity Standards, QCS-27. The concentration of calibration standard was 5 ppb. Calibration was done with three standards which were 1 ppb, 3 ppb and 5 ppb. The analyzer was able to dilute 5ppb to 1 ppb and 3ppb.So, in the analysis, only one calibration standard (5 ppb) was prepared. In addition, blank sample (0.2 % HNO_3, v/v) was also prepared. A matrix modifier was used in this analysis to eliminate interferences. As matrix modifiers, Palladium and Mg $(NO_3)_2$ were used and prepared according to technical note provide by Perkin Elmer. 5 mL Pd (1%) standard (Perkin Elmer) and 3 mL Mg $(NO_3)_2$ (1%) were prepared for this analysis. Blank samples, calibration standard, matrix modifier, and samples were put into the auto sampler tray in order and the analysis was conducted. First, blank sample and calibration standards were measured and calibration curve was formed with a correlation of 0.984. During sample analysis, the samples were diluted in the ratio of 1/20 automatically to be able to read by the analyzer (Method 3113 B) (Perkin Elmer, 2003; APHA, AWWA, WEF, 2005).

3.1.3.3. PCB Extraction and Analysis Procedure

A 0.5 g of freeze-dried sludge was added into a 22-mL glass vial. Glass vial was sealed with PTFE screw cap. As extraction solvent, n-hexane was used and extraction was carried out on a shaker by shaking the samples for 16 hours. PCB analysis was done with GC/ECD (Agilent/6890 N) and the concentration was determined by the use of a previously prepared calibration curve. Other details of the procedure can be found at Kaya (2012).

3.1.3.4. NPE Extraction and Analysis Procedure

A 0.5 g freeze dried samples was added into a 12-mL amber vial. Then, the sample was extracted with sonication based extraction method (5 min) using acetone as solvent. In addition, samples were derivatized by BSTFA +TMCS. For analysis, GC-MS was used. A previously prepared calibration curve was used for the determination of concentrations. NPE which is the sum of NP, NP1EO and NP2EO was measured. Other details can be found at Ömeroğlu (2012).

3.2. Health Risk Assessment Methodologies Followed in This Study

Health risk assessment study for the land application of biosolids originating from ACWWTP was carried out using two different methodologies as also mentioned above; U.S. EPA's and INERIS's. First, the health risk assessment study conducted according to U.S. EPA's methodology is explained.

3.2.1. Application of U.S. EPA's Health Risk Assessment Methodology for Sludge Samples of ACWWTP

As mentioned in Section 2.6.1.1, this is a four-step procedure. Below is a discussion of the work done under this four-step procedure.

3.2.1.1. Hazard Identification

In the hazard identification step, the contaminants of concern (COC) needed to be selected and identified. In this study, both heavy metals and selected organic pollutants were included within the

scope of Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010). Seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) and two of the organic pollutants (PCBs and NPEs) which were readily measurable in laboratories of METU Environmental Engineering Department were chosen. The pollutants are listed in Table 3.2. The other trace organic pollutants were not taken into consideration since the equipments and methods for the analysis were not available in the department.

Table 3.2: Pollutants Chosen in Hazard Identification

Inorganic Pollutants	Organic Pollutants
Cd	PCBs
Cr	NPEs
Cu	
Hg	
Ni	
Pb	
Zn	

3.2.1.2. Exposure Assessment

U.S EPA identified 14 pathways in total (See Table 2.5). Out of 14 pathways, Pathway 3 (child ingesting biosolids) is one of the most limiting pathways included in U.S. EPA's method and also it is the most limiting pathway for human health in terms of heavy metals (See Table 2.6). Most limiting pathways in U.S. EPA's study were chosen according to lowest-risk based pollutant limits for each pollutant comparing all risk-based pollutant limits for all pathways (U.S. EPA, 1995). Pathway 3 does not require any site specific parameters to calculate health risks. Therefore, Pathway 3 was selected in this study to calculate associated health risks due land application of biosolids.

One of the other limiting pathways (Pathway 8), which is 'plant phytotoxicity' were not included in this study. To calculate risks for Pathway 8, threshold phytotoxic concentration of pollutants in plant tissue and uptake slope of pollutants should be known. However, required data were not available during the study. Additionally, this pathway determines the toxic effects of biosolids application on the growth of plants. Main goal of this study is to evaluate possible health risks on humans. Thus, Pathway 8 was not taken into account in this study.

In this study, the ingestion of biosolids by a child was assumed to last for five years and is associated with two possible scenarios (U.S. EPA, 1992). Biosolids can be ingested by a child from the surface of land which biosolids are applied or can be ingested from a bag or container near to land application area which includes biosolids. For both scenarios, it was assumed that biosolids is undiluted and directly ingested by a child. It was also assumed that soil and other materials are not ingested by a child during ingestion of biosolids(Figure 3.4).

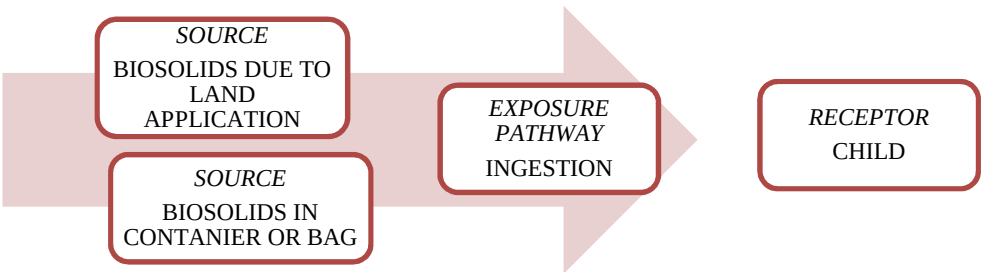

Figure 3.4: Conceptual Scheme of the Exposure Assessment for Land Application of Biosolids Originating from ACWWTP with U.S. EPA's Method

3.2.1.3. Dose-Response Evaluation

In this study, for the calculation of non-cancer risks, RfD values (See Equation 2.1) were used. On the other hand, for the calculation of cancer risks, q_1^* values (See Equation 2.2) were used. Heavy metals and organic pollutants may have non-cancer and/or cancer effects. For the selected heavy metals in this study, only non-cancer effects are observed according to US EPA IRIS database and for most of the heavy metals RfD values are available (Table 3.3). For copper, RfD is not available in U.S. EPA IRIS database. However, Recommended Dietary Allowance (RDA) value for copper is determined as 0.125 mg/kg.day (U.S. EPA, 1992). This value was used in this study as suggested by U.S. EPA (1992). Additionally, for lead, there is no RfD value provided in U.S. EPA IRIS database and U.S. EPA documents.

For organic pollutants including PCBs and NPEs, there are no RfD values available in U.S. EPA's IRIS database or any U.S. EPA document. Therefore, non-cancer risk calculations were not conducted for PCBs and NPEs. For cancer-risk calculations, q_1^* is only available for PCB. Therefore, cancer risk calculations were done only for PCB.

Table 3.3: RfD and q_1^* Values of Heavy Metals and Organic Pollutants (U.S. EPA IRIS and U.S. EPA, 1992)

Pollutant	RfD **(mg/kg.day)**	q_1^* **(mg/kg.day)$^{-1}$**
Cd	0.001	-
Cr	1.5	-
Cu	0.125	-
Hg	0.0003	-
Ni	0.02	-
Pb	-	-
Zn	0.625	-
PCB	-	7.7
NPE	-	-

-: data not available

3.2.1.4. Risk Characterization

In this study, both non-cancer and cancer risks were calculated in risk characterization step. As discussed above, non-cancer risks were calculated for only heavy metals except for Pb and cancer risks were calculated only for PCBs.

Non-Cancer Risk Calculations

In this step of the study, for non-cancer risks using equation 2.1, HI values were calculated. However, in biosolids, there is more than one pollutant and the HI values should be summed up to determine the cumulative non-cancer effects. In U.S. EPA's study, pollutant limits were determined assuming that HI is equal to one for each pollutant. However, if biosolids are ingested by a child, not only one pollutant, all pollutants enter the body of the child and the child is affected by all pollutants. Therefore, non-cancer risks should be summed up (U.S.EPA, 2007b). In this study, for a single exposure pathway and multiple chemicals 'Cumulative Hazard Index' term was used with an abbreviation of $\sum HI$.

$\sum HI$ can be found using the formula below (U.S.EPA, 2007b):

$$\sum HI = \sum_{j=1}^{n} HIj \tag{3.1}$$

Where j is chemical and n is the number of chemicals in the assessment. $\sum HI$value is analyzed whether it is less than 1 or not. If $\sum HI$ is less than 1, adverse effects of concentration of the pollutant areconsidered to be insignificant for the receptor. Conversely, if $\sum HI$ is more than 1, adverse effects of the pollutant may be concern for the receptor. For this situation, a more detailed analysis should be conducted for the determination of chemicals in which drives the risk indicator (U.S. EPA, 2007b).

For the calculation of HI and $\sum HI$, assumptions used by U.S. EPA (1992) were applied in this study. Soil ingestion rate was taken as 0.2 g/day and body weight of a child was taken as 16 kg. In addition, DE and RE values were also taken as 1. As contaminant concentrations, the concentrations in sludge samples of ACWWTP were used (Figure 4.1). For all heavy metals apart from Pb, the HI values were calculated. The results arepresented and discussed in detail in Section 4.2.1.1

Limit values provided in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010) were also analyzed in terms of non-cancer effects. $HI$and $\sum HI$values of this section are presented and discussed in Section 4.2.1.3.

Cancer Risk Calculations

$Risk$ valueswere determined by using Equation 2.2. Soil ingestion rate was taken as 0.2 g/day and body weight of a child was assumed as 16 kg. Furthermore, DE was taken as 0.0714 and RE was also set to 1 as suggested by U.S. EPA (1992). The Risk values are presented and discussed in Section 4.2.1.2.

As non-cancer risks, cancer risks also can be summed up and cumulative cancer risk can be found. The following equation is used for cumulative cancer risk calculation (U.S. EPA, 1989):

$$Risk_T = \sum Risk_i \tag{3.2}$$

$Risk_T$: the total cancer risk
$Risk_i$: the risk estimated of the i[th] substance

In this study, for cancer risks, $Risk$ was evaluated only for PCBs since only PCBs has q_1^* value among other selected pollutants (See Table 3.3). Therefore,$\sum Risk_i$values were not calculated for this study.

In addition to calculation of cancer risks of biosolids originating from ACWWTP, PCBs limit value provided in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010) was also analyzed in terms of cancer effects. $Risk$ value for the PCBs limit value is presented and discussed in Section 4.2.1.3

3.2.2. Application of INERIS's Health Risk Assessment Methodology for Sludge Samples of ACWWTP

In this study, as a second approach, the method used by INERIS was followed and the following four-step procedure was analyzed in detail.

3.2.2.1. Substance Selection

In this step, same methodology used in step 1 of EPA's method was followed. Thus, the pollutants given in Table 3.2 were selected as substances of concern.

3.2.2.2. Toxicity Evaluation

For the selected heavy metals in this study, TRV for threshold (non-cancer) effects (mg/kg.day)values are available and given in Table 3.4. However, non-threshold effects cannot be calculated for selected heavy metals since TRV values for non-threshold effects $(mg/kg.day)^{-1}$ are not available.

For the selected organic pollutants, $TRVs$ for threshold effects (mg/kg.day) are available and threshold effects were evaluated for PCBs and NPEs in this study. On the other hand, $TRVs$ for non-threshold (cancer) effects $(mg/kg.day)^{-1}$ are only available for PCBs (Table 3.4). Therefore, non-threshold effects were calculated only for PCBs.

Table 3.4: TRVs for Threshold Effects and TRVs for Non-Threshold Effects of Selected Heavy Metals and Organic Pollutants (INERIS, 2008)

Pollutant	TRV for threshold effects (mg/kg.day)	TRV for non-threshold effects $(mg/kg.day)^{-1}$
Cd	0.001	-
Cr	1.5	-
Cu	0.14	-
Hg	0.0001	-
Ni	0.02	-
Pb	0.0035	-
Zn	0.3	-
PCB	0.00002	2
NPE	0.0045	-

3.2.2.3. Exposure Evaluation

Receptor and Pathway Determination

INERIS identified 12 pathways for land spreading of sludge (See Table 2.8). In this study, out of 12 pathways, only one pathway, which is ingestion of soil amended with sludge by a child, was selected. For other pathways, there were no available site-specific data to calculate associated health risks.

This pathway is different from the pathway chosen in U.S. EPA's method in terms of source of the exposure. In this pathway, child ingests soil mixed with sludge (Figure 3.5). On the other hand, in the pathway of U.S. EPA's method, the child ingests biosolids directly without dilution.

Figure 3.5: Conceptual Scheme of the Exposure Assessment for Land Application of Biosolids Originating from ACWWTP with INERIS's Method

Substance Concentrations

In this study, substance concentrations are calculated using Equation 2.5. Background soil concentrations are taken from the literature. Bilgin *et al.*(2002) provided two types of soil pollutant concentrations (i.e. minimum and maximum) which belong to soils near ACWWTP (Table 3.5). In this study, maximum concentrations were taken into account to be more conservative. For PCBs and NPEssoil concentrations are assumed to be zero since no measurements are available.

Table 3.5: Background Soil Concentrations near ACWWTP (Bilgin *et al.*,2002)

Pollutant	Minimum Soil Concentration (mg/kg)	Maximum Soil Concentration (mg/kg)
Cd	0.16	0.24
Cr	33.7	137
Cu	26.9	42.5
Ni	24.8	198
Hg	0.02	0.08
Pb	7.02	13.03
Zn	41.0	54.1

To determine cumulative sludge concentrations, Dilution Factor (DF), degredation and cumulative inputs of pollutants in sludge were taken into account. In Turkey, land application of biosolids is not very common and there is no data for land application rate for biosolids. To calculate Dilution Factor (DF), same assumptions provided by INERIS (2008) were used and application rate was taken as 3 tons/ha.year, Additionally, the soil depth was taken as 0.25 cm, and the soil bulk density was taken as 1.3 tons/m^3. With these assumptions dilution factor (DF) was calculated using Equation 2.3. For degradation, among selected pollutants, it was taken into account only for NPE and half-life of NPE was taken as 0.41 day^{-1}. Degraded concentrations of NPE were calculated by Equation 2.4. To determine cumulative inputs of pollutants in sludge, it was also assumed that sludge is applied to the soil during 70 years and child exposure occurs during last years of application to be conservative. It means, between 65^{th} and 70^{th} years, the child exposed to soil amended with sludge. This assumption was also used by INERIS for child exposure. Cumulative sludge concentrations were calculated for between 65^{th} and 70^{th} years (for 6 years) considering dilution factor and degradation. Then, average cumulative sludge concentration was determined using calculated cumulative sludge concentrations between 65^{th} and 70^{th} years. Finally, Substance Concentrations were calculated for each selected pollutant (See Equation 2.5). The results of substance concentrations are given in Section 4.2.2.

Exposure Equations

In this section, Equation 2.6 was used to define Daily Exposure Dose(DED) foreach pollutant assuming that mass of soil ingestion as 150 mg/day and exposure frequency is 0.021.The calculated *DED* values are presented and discussed in Section 4.2.2.

3.2.2.4. Risk Calculation

Risk calculations were processed using Equation 2.7 for threshold effects and Equation 2.8 for non-threshold effects. Moreover, $\sum HI$ or $\sum ER$ values were calculated in this study for the ingestion of soil amended sludge by a child pathway. The results are provided and discussed in Section 4.2.2.1. and 4.2.2.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Pollutant Concentrations in Sludge Samples

In this study, for the calculation of health risks, pollutant concentrations in sludge samples should be known. Measured concentrations of seven heavy metals (Cd, Cr, Cu, Hg, N, Pb and Zn), PCBs and NPEs in sludge samples originating from ACWWTP are presented and discussed in detail in the following sections.

4.1.1. Heavy Metal Concentrations in Sludge Samples

In ACWWTP, 10% of wastewater entering the treatment plant is industrial wastewater. Industrial wastewater originates from Sincan OSB, zinc-plating, metal industry, mine industry, and textile industry. These industries are the main sources for heavy metal concentrations in sludge of the ACWWTP.

Heavy metal concentrations were analyzed in triplicate samples and for each sample, Atomic Absorption Spectrometry (AAS) processed three concentrations which means for each sample, nine heavy metal concentration values were measured. Average concentrations and standard deviations of selected heavy metals on yearly basis are given in Figure 4.1. In addition, the pollutant limit values for sludge provided in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010) are given in each figure at the top of the x-axis (See Figure 4.1) As can be seen from the Figure 4.1, the standard deviation values are usually very low showing the reproducibility of the measurements. The results also show that in a one year time frame, heavy metals concentrations in samples show some fluctuations. In addition, no common trend for all heavy metal concentrations can be observed monthly or seasonally. Irregular heavy metal inputs from the industries may be the reason for observing such differences in trends between heavy metals and fluctuations in heavy metal concentrations.

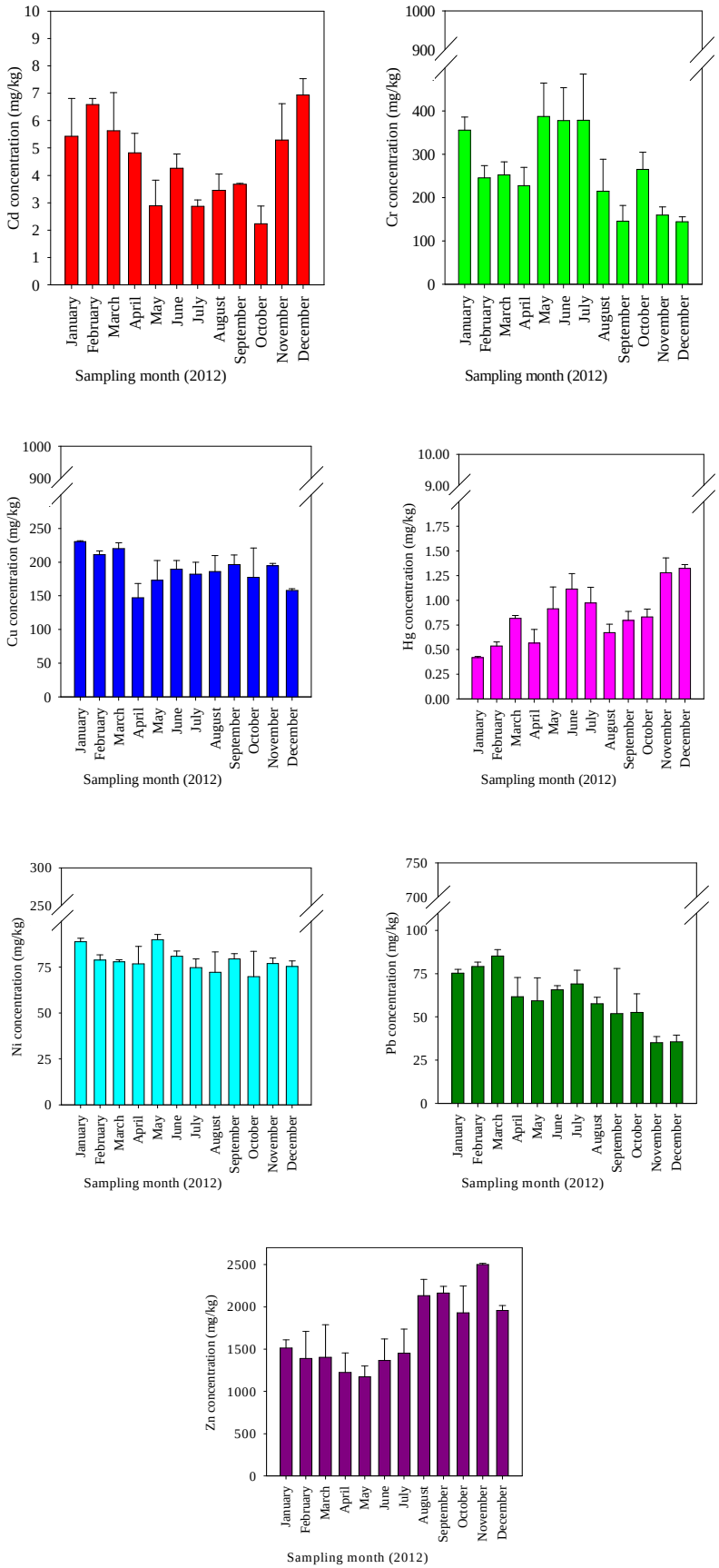

Figure 4.1: Graphical Demonstrations of Heavy Metal Concentrations in Sludge Samples (mg/kg)

Table 4.1: Minimum, Average and Maximum Concentrations of Heavy Metals for 12-monthly Samples

Heavy Metal	Minimum Concentration (mg/kg)	Average Concentration (mg/kg)	Maximum Concentration (mg/kg)	Standard Deviations	Pollutant Limit Values(mg/kg)*
Cd	2.3	4.5	6.9	0.7	10
Cr	144.0	262.9	356.1	47.6	1000
Cu	147.1	188.8	230.3	15.4	1000
Hg	0.4	0.8	1.3	0.1	10
Ni	69.7	78.4	89.9	5.0	300
Pb	35.1	60.7	85.2	15.6	750
Zn	1174.7	1683.8	2499.9	195.9	2500

**Limit values are taken from Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010)*

To be suitable for use in agriculture, heavy metal concentrations in the samples should be below the limit values given in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010). According to the results, the concentrations of Cd, which is one of the most critical metals in sludge concerning land application, vary between 2.3 and 6.9 mg/kg (Table 4.1). Especially in winter, the concentrations are higher when compared to the other months. However, no Cd concentrations exceed limit value for Cd (10 mg/kg) given in the regulation.

The measured concentrations range for Cr is 144 mg/kg to 356.1 mg/kg (Table 4.1). Cr concentrations are observed as higher in May, June and July. In the other months, the concentrations are much lower and all the concentrations are below the limit value for Cr (1000 mg/kg) given in the regulation. Cr concentrations can be considered as safe for land application of biosolids when they are compared with the limit value.

Cu concentrations are measured between 147.1 mg/kg and 230.3 mg/kg (Table 4.1). Measured Cu concentrations are higher in the first three months of the year which are January, February and March. Similar to Cr, all measured Cu concentrations are also much lower than the limit value (1000 mg/kg).

Hg is one of the other heavy metals concentrations of which were measured in samples. Hg concentrations vary between 0.4 mg/kg and 1.3 mg/kg (Table 4.1). The higher concentrations are observed in December and November. Similar to other heavy metals, all measured Hg concentrations are also below the Hg limit value (10 mg/kg) given in the regulation.

Ni concentrations are observed between 69.7 mg/kg and 89.9 mg/kg (Table 4.1) and not showing a wide range. The highest Ni concentration belongs to May. The limit value for Ni given in the regulation is 300 mg/kg and according to the results, Ni concentrations are not seen problematic for land application.

Pb concentrations are between 35.1 mg/kg and 85.2 mg/kg(Table 4.1). Decreases in Pb concentrations are observed from the first month of the year to the last month of the year. As the Pb concentrations are compared with the limit value (750 mg/kg) given in the regulation, it is obvious that all Pb concentrations are much lower than the limit value for Pb.

Finally, Zn concentrations vary between 1174.7 mg/kg and 2499.9 mg/kg (Table 4.1). The Zn concentration increases sharply in August and higher Zn concentrations are observed from August to December. The highest Zn concentration belongs to November, which is approximately 2500 mg/kg. In addition, in September and October, the concentrations are more than 2100 mg/kg and approach to the limit value (2500 mg/kg). The findings of this study show that Zn seems to be the most critical pollutant for land application. Zn concentrations should be followed carefully before land application in order to check the compliance with the regulation.

The measured concentrations were also compared with similar studies found in the literature. Özsoy (2006) conducted a study to evaluate agricultural potential of four wastewater treatment plants including ACWWTP in terms of heavy metals and pathogens between 2005 and 2006The results of this study show resemblances except for Zn. Zn concentrations were observed between 1695 mg/kg

and 4065 mg/kg in Özsoy (2006). However, in this study, the highest Zn concentration is approximately 2500 mg/kg. Such a decrease in Zn concentrations may be due to advances in application of treatment technologies or changes in operation processes of the industries which discharge their wastewater into the wastewater collection system of Ankara. In addition, Ankara Water and Sewerage Administration (ASKİ) may have set stricter control limits for industries in terms of heavy metals to discharge their wastewaters.

4.1.2. PCB Concentrations in Sludge Samples

PCB concentrations were measured as congener based. The measured concentrations include sum of seven congeners (PCB-28, PCB-52, PCB-101, PCB-118, PCB-153, PCB-138, and PCB-180).The concentrations range between 0.004 mg/kg and 0.06 mg/kg (Figure 4.2). According to the results, in summer months (June, July and August, 2012), the concentrations are higher when compared to results from other months. However, all the concentrations are below the limit value (0.8 mg/kg, sum of the same seven congeners) set in the Turkish Regulation.

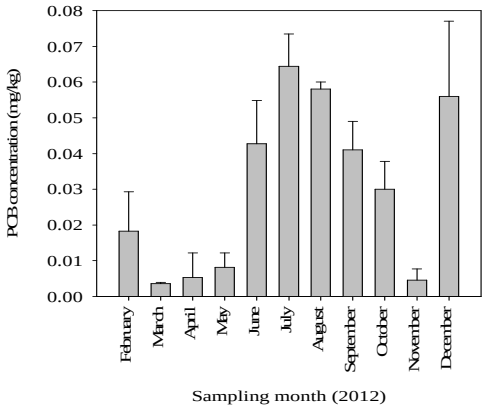

Figure 4.2: Graphical Demonstration of PCB Concentrations in Sludge Samples (mg/kg)

4.1.3. NPE Concentrations in Sludge Samples

NPE concentrations (sum of NP, NP1EO and NP2EO) for sludge samples were analyzed and the results are given in Figure 4.3. NPEs concentrations vary between 5.3 mg/kg and 25.5 mg/kg. After August, a sharp increase is observed. The highest NPEs concentration belongs to November. As the NPEs concentrations are compared with the limit value (50 mg/kg, sum of NP, NP1EO and NP2EO) set in Turkish Regulation, it is obvious that all concentrations are below the limit value.

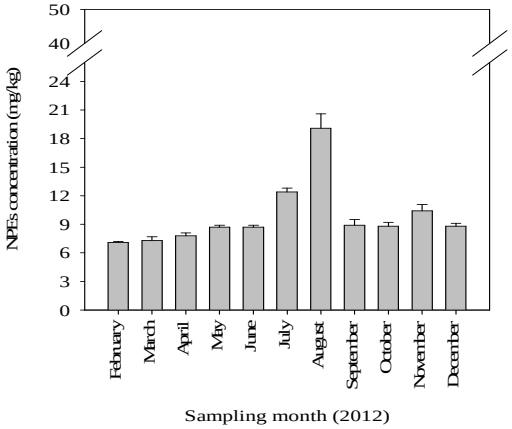

Figure 4.3: Graphical Demonstrations of NPE Concentrations in Sludge Samples (mg/kg)

4.2. Results of Health Risk Calculations

In this study, health risk calculations due to land application of biosolids originating from ACWWTP were conducted using two different methodologies (U.S. EPA and INERIS) for both cancer and non-cancer effects as mentioned before. The results of the health risk calculations for both methodologies are given and discussed below.

4.2.1. Health Risk Calculations with U.S. EPA's Method

Health risks due to land application of biosolids were calculated in the current study only for the ingestion of biosolids by a child pathway. Health risk calculations were performed for six heavy metals (Cd, Cr, Cu, Hg, Ni and Zn) for non-cancer effects. Moreover, cancer risks were calculated for PCBs. For Pb and NPEs, neither cancer nor non-cancer risks were calculated due to lack of RfD andq_1^* values in U.S. EPA IRIS database (See Section 3.2.1.3).

4.2.1.1. Health Risk Calculations for Non-Cancer Effects

In this section, first, HI values were calculated for each sample and each heavy metal for non-cancer effects. The results are given in Figure 4.4 and detailed calculations are given in Appendix B. The results of non-cancer risks showed thatHIvalues of Cr were approximately an order of magnitude lower than the HIvalues of the other heavy metals.HIvalues of Cu were also considered low when compared to other heavy metals. Highest HI values were observed for Cd and Ni among all the heavy metals. HIvalues of Hg were also high even though the Hg concentrations in sludge samples were the lowest among other heavy metals. Additionally, although Zn concentrations were much higher when compared to other heavy metals, the HIvalues of Zn were lower thanHIvalues of Ni and Cd. As can be seen from Figure 4.1, higher concentrations are not associated with higher HI values of different heavy metals. This is due to different RfD values of different heavy metals.

As the second step, all HIvalues of heavy metals were summed up to determine cumulative non-cancer effects for each sampling month and $\sum HI$values were calculated (See Section 3.2.1.4 for details). The $\sum HI$ results and contribution of each heavy metal to$\sum HI$are given in Figure 4.4. $\sum HI$values vary between 0.16 and 0.25. The highest $\sum HI$value is observed in December.

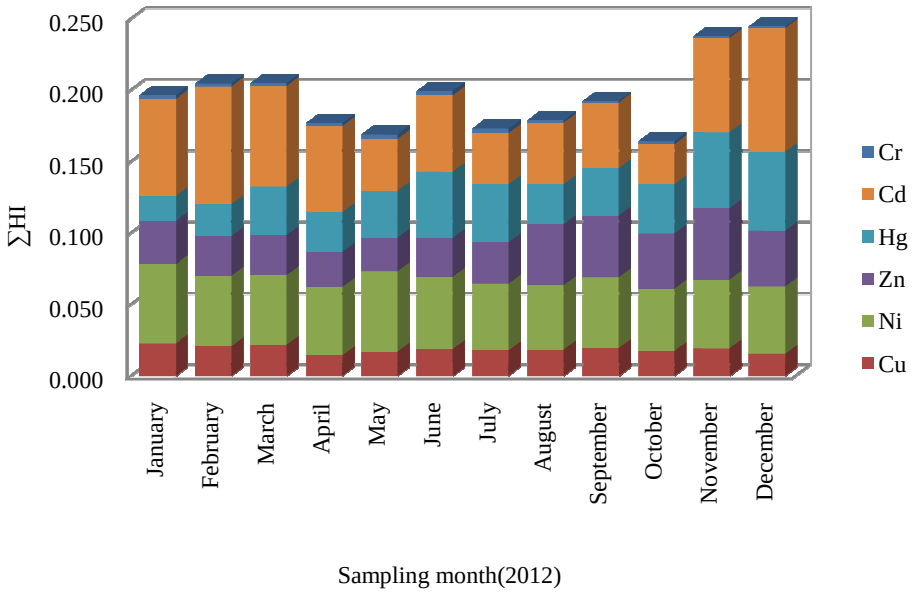

Figure 4.4: $\sum HI$ Values and Contributions of Heavy Metals to$\sum HI$

$\sum HI$ values should be checked whether they are more than 1 or not (U.S. EPA, 2007b).According to the results, the calculated values are much lower than 1. It can be concluded from these results thatadverse non-cancer effects of heavy metals in sludge samples originating from ACWWTP are not significant to develop for a child who ingests biosolids. However, it does not mean that the land application of biosolids does not result in any non-cancer effects for the child since, this study only indicates $\sum HI$ due to ingestion of biosolids. The child may also consume plants which are grown on soil amended with biosolids, or may consume animal products which are affected by biosolids. Hence, if site-specific data are available, all pathways should be considered as a whole and health risk calculations should be carried out considering all pathways.

4.2.1.2. Health Risk Calculations for Cancer Effects

In this section, *Risk* values were calculated for PCBs (Figure 4.5) only for child ingesting biosolids pathway and given in detail in Appendix B. According to Figure 4.5, the *Risk* values vary between $3.9*10^{-7}$ and $2.5*10^{-8}$. These values are very low when compared to the acceptable risk level (10^{-4}) selected by U.S. EPA in cancer risk calculations for the land application of biosolids (U.S. EPA, 1995).

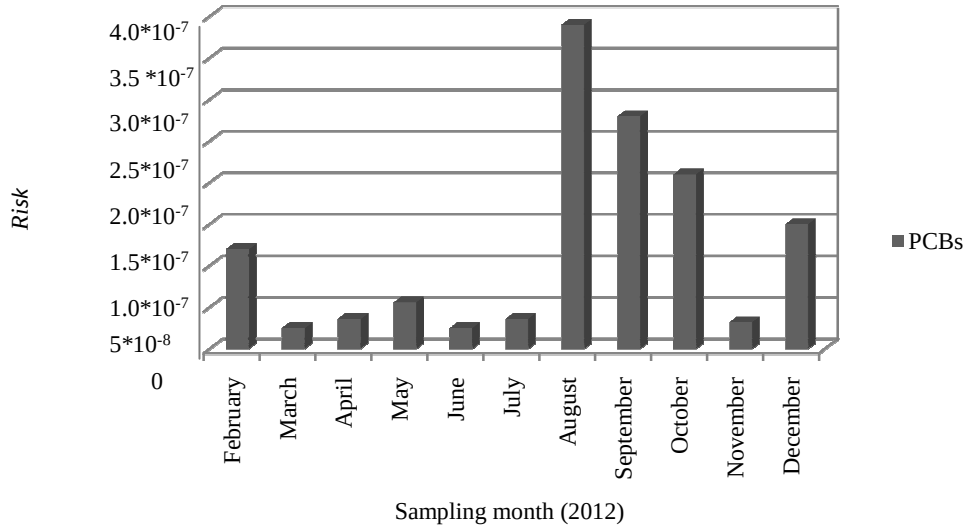

Figure 4.5: *Risk* Values for Sludge Samples of ACWWTP

Generally, U.S. EPA uses acceptable risk levels between 10^{-4} and 10^{-6} in cancer risk studies (National Research Council, 2002). Even if an acceptable risk level of 10^{-6} is chosen for ingestion of biosolids by a child pathway, the *Risk*values will under this acceptable risk level. It means cancer effects are not considered to be significant for child due to PCBs for ingestion of biosolids pathway alone.

4.2.1.3. Health Risk Calculations for Limit Values Given in Turkish Regulation for the Use of Sewage Sludge in Agriculture with U.S. EPA's Method

The non-cancer and cancer risks were calculated for the sludge samples of ACWWTP and results showed that the land application of biosolids would not result in significant health risks due to ingestion of biosolids by a child pathway.

Here, health risks were also determined for limit values provided in Turkish Regulation for the Use of Sewage Sludge in Agriculture related to the land application of biosolids in order to evaluate whether

the regulatory limit values are adequately protective for human health. For health risk calculations, only child ingesting biosolids pathway was included in this study due to one of the limiting pathways in U.S. EPA's method and not requiring any site-specific data (See Section 3.2.1.2). In addition, the pollutants included within the scope of this study (See Table 3.2) were selected and their limit values were taken as pollutant concentrations (See Table 2.1).Associated health risks were calculated for ingestion of biosolids by a child pathway with U.S. EPA's method. During calculations same RfD and q_1^* values were used (See Table 3.3).Non-cancer risk calculations were conducted for seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) and given in detail in Appendix B. *HI* values were calculated for each limit value and they were summed up to determine $\sum HI$. Furthermore, cancer risk calculations were conducted for limit value of PCBs and given in detail in Appendix B.

According to the results of non-cancer risks (Figure 4.6), the highest *HI* value is observed for Hg, which is followed by Ni, Cd and Cu. After calculating *HI* values for each heavy metal, they were summed up and $\sum HI$ was determined as 0.89. This value is very high when compared to $\sum HI$ values obtained for sludge samples from ACWWTP. However, it is less than one, which means adverse non-cancer health effects are not considered to be significant for child. Apart from child ingesting of biosolids pathway, there are other pathways (See Table 2.5) which child may be exposed to heavy metals in biosolids due to land application. Other pathways are not the concern of this study; however, it is important to mention that they should also be evaluated to be able to see cumulative health risks for child due to multiple exposure pathways.

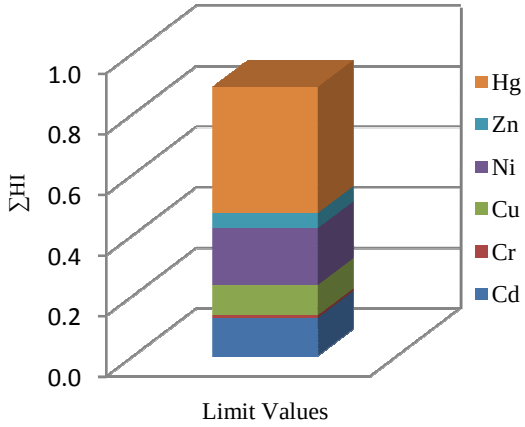

Figure 4.6: $\sum HI$ Value for Limit Values in Turkish Regulation for the Use of Sewage Sludge in Agriculture

Risk for PCB was also calculated as $5.5*10^{-6}$ using the limit value provided in the regulation only for child ingesting biosolids pathway. This cancer risk is lower than the acceptable risk level suggested by U.S. EPA (1995) which is 10^{-4}. With this acceptable risk level, it can be concluded that cancer risks are considered as insignificant for child ingesting biosolids pathway alone. However, as stated before, acceptable risk levels can be between 10^{-4} and 10^{-6} (National Research Council, 2002). If risk level is chosen as 10^{-6}, the result is higher than the risk level and becomes a concern for the child's health. In addition, cancer risks associated PCBs intakes due to other pathways are not considered here. This fact should be kept in mind. If the acceptable risk is chosen as 10^{-6}, the limit value for PCBs will not be protective for child health associated with land application of biosolids only one pathway is considered. Thus, more detailed studies for PCBs is required to assess cancer risks associated with land application of biosolids.

4.2.2. Health Risk Calculations with INERIS's Method

In this section, health risks for both threshold (non-cancer) effects and non-threshold (cancer) effects due to land spreading of sludge were calculated only for ingestion of soil which is mixed with sludge by a child. For calculation of health risks, first, average substance concentrations were calculated (See

Section 3.2.2.3 for details). The results are given for heavy metals and organic pollutants in Table 4.2 and Table 4.3, respectively.

The results for both heavy metals and organic pollutant suggested that average substance concentrations in soil mixed with sludge were much lower than pollutant concentrations in sludge due to dilution of pollutants in soil (one of the distinct assumptions of the method). For NPE, degradation was also taken into account as well and the concentrations were further lowered (See Section 3.2.2.3).

Table 4.2: Average Substance Concentrations for Heavy Metals in Soil Mixed with Sludge Samples of ACWWTP (mg/kg)

Sampling Month (2012)	**Heavy Metal Concentrations (mg/kg)**						
	Cd	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
January	0.59	160.01	57.38	0.11	203.73	17.86	151.9
February	0.66	152.89	56.13	0.11	203.09	18.11	143.9
March	0.60	153.31	56.62	0.13	203.03	18.51	144.8
April	0.55	151.71	52.01	0.12	202.95	17.99	133.2
May	0.42	155.58	53.69	0.14	203.80	16.84	130.0
June	0.51	161.46	54.74	0.15	203.23	17.24	142.5
July	0.42	161.51	54.27	0.14	203.11	17.65	147.5
August	0.46	150.79	54.51	0.12	202.65	16.73	191.6
September	0.48	146.41	55.21	0.13	203.13	16.36	194.1
October	0.38	154.16	53.94	0.13	203.49	16.40	178.5
November	0.58	147.24	55.09	0.16	202.97	15.26	215.6
December	0.69	146.30	52.71	0.17	202.97	15.30	180.5

Table 4.3: Average Substance Concentrations for Organic Pollutants in Soil Mixed with Sludge Samples of ACWWTP (mg/kg)

Sampling Month (2012)	**Organic Pollutant Concentrations (mg/kg)**	
	PCB	**NPE**
February	0.0011	0.0077
March	0.0002	0.0080
April	0.0003	0.0086
May	0.0005	0.0096
June	0.0027	0.0096
July	0.0040	0.0136
August	0.0037	0.0219
September	0.0026	0.0097
October	0.0019	0.0097
November	0.0003	0.0114
December	0.0013	0.0096

Substance concentrations for selected pollutants were determined to calculate Daily Exposure Dose (DED) values. DED values using Equation 2.6 are calculated and presented in Table 4.4. According to the results, the DED values change between 10^{-5} and 10^{-10} mg/kg.day.

Table 4.4: DED Values for Heavy Metals and Organic Pollutants in Soil Mixed with Sludge Samples of ACWWTP

Sampling Month (2012)	***DED* Values (mg/kg.day)**								
	Cd	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**PCB**	**NPE**
January	$1.2*10^{-7}$	$3.4*10^{-5}$	$1.2*10^{-5}$	$2.2*10^{-8}$	$4.3*10^{-5}$	$3.8*10^{-6}$	$3.9*10^{-5}$	-	-
February	$1.4*10^{-7}$	$3.2*10^{-5}$	$1.2*10^{-5}$	$2.5*10^{-8}$	$4.3*10^{-5}$	$3.8*10^{-6}$	$3.0*10^{-5}$	$2.5*10^{-10}$	$1.6*10^{-9}$
March	$1.2*10^{-7}$	$3.2*10^{-5}$	$1.2*10^{-5}$	$2.8*10^{-8}$	$4.3*10^{-5}$	$3.9*10^{-6}$	$3.0*10^{-5}$	$4.9*10^{-11}$	$1.7*10^{-9}$
April	$1.1*10^{-7}$	$3.2*10^{-5}$	$1.1*10^{-5}$	$2.5*10^{-8}$	$4.3*10^{-5}$	$3.6*10^{-6}$	$2.8*10^{-5}$	$7.2*10^{-11}$	$1.8*10^{-9}$
May	$8.9*10^{-8}$	$3.2*10^{-5}$	$1.1*10^{-5}$	$2.9*10^{-8}$	$4.3*10^{-5}$	$3.5*10^{-6}$	$2.7*10^{-5}$	$1.1*10^{-10}$	$2.0*10^{-9}$
June	$1.1*10^{-7}$	$3.4*10^{-5}$	$1.2*10^{-5}$	$3.2*10^{-8}$	$4.3*10^{-5}$	$3.6*10^{-6}$	$2.9*10^{-5}$	$5.8*10^{-10}$	$2.0*10^{-9}$
July	$8.9*10^{-8}$	$3.4*10^{-5}$	$1.1*10^{-5}$	$3.0*10^{-8}$	$4.3*10^{-5}$	$3.7*10^{-6}$	$3.1*10^{-5}$	$8.7*10^{-10}$	$2.9*10^{-9}$
August	$9.7*10^{-8}$	$3.2*10^{-5}$	$1.1*10^{-5}$	$2.6*10^{-8}$	$4.3*10^{-5}$	$3.5*10^{-6}$	$4.0*10^{-5}$	$7.8*10^{-10}$	$4.4*10^{-9}$
September	$1.1*10^{-7}$	$3.1*10^{-5}$	$1.2*10^{-5}$	$2.7*10^{-8}$	$4.3*10^{-5}$	$3.4*10^{-6}$	$4.1*10^{-5}$	$5.6*10^{-10}$	$2.0*10^{-9}$
October	$8.0*10^{-8}$	$3.2*10^{-5}$	$1.1*10^{-5}$	$2.8*10^{-8}$	$4.3*10^{-5}$	$3.5*10^{-6}$	$3.7*10^{-5}$	$4.1*10^{-10}$	$2.0*10^{-9}$
November	$1.2*10^{-7}$	$3.1*10^{-5}$	$1.2*10^{-5}$	$3.4*10^{-8}$	$4.3*10^{-5}$	$3.2*10^{-6}$	$4.5*10^{-5}$	$6.2*10^{-11}$	$2.4*10^{-9}$
December	$1.4*10^{-7}$	$3.1*10^{-5}$	$1.1*10^{-5}$	$3.5*10^{-8}$	$4.3*10^{-5}$	$3.2*10^{-6}$	$3.8*10^{-5}$	$2.8*10^{-10}$	$2.0*10^{-9}$

4.2.2.1. Health Risk Calculations for Threshold (Non-Cancer) Effects

In this section, health risks were calculated through HI values for threshold effects for only child ingesting soil mixed with sludge pathway (Figure 4.7 and See Appendix C).Variations on HI values for each pollutant are directly related to average substance concentrations. NPEs have the lowest HI values among other pollutants. HI values of NPEs were only calculated with INERIS's method. In U.S. EPA's method, RfD value for NPEs was not suggested. Most critical pollutant for threshold effects is Ni since it has the highest HI values.

HI values were summed up for each sampling month and $\sum HI$ data were obtained. The results of$\sum HI$ values are given in Figure 4.7. According to $\sum HI$ results, the values vary between 0.0035 and 0.0038. Highest $\sum HI$ is observed for March. In U.S. EPA's method the highest $\sum HI$ belonged to December. The main reason for such a difference is that, TRV of RfD values were used in risk calculations which have different values for some of the heavy metals such as Hg, Cu and Zn. In addition, non-cancer risks related to Pb and NPE were included in INERIS's method and consideration of Pb in calculations may also result in such a difference.

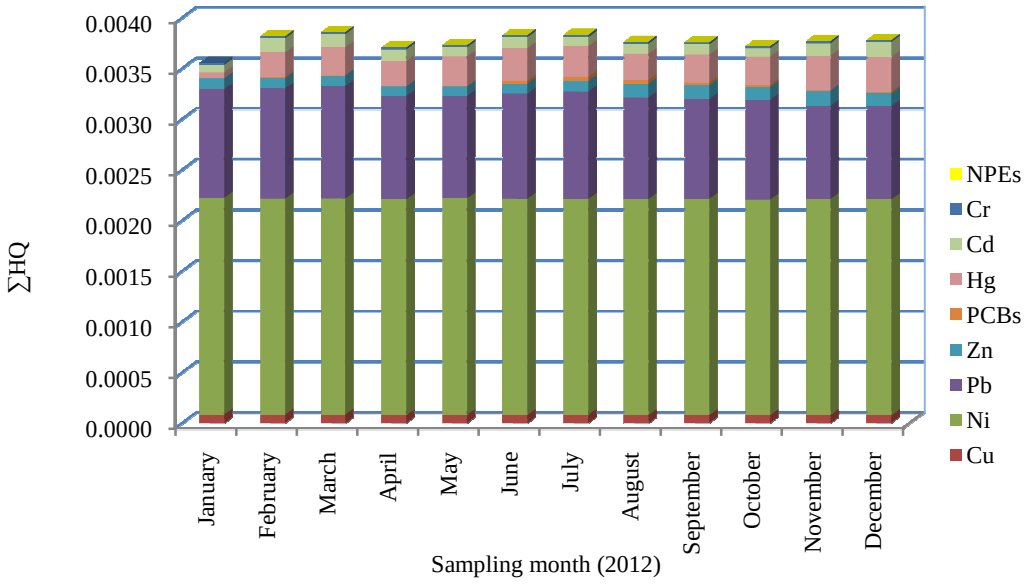

Figure 4.7: $\sum HI$ Values and Contributions of the Selected Pollutants to $\sum HI$

$\sum HI$ values should be compared whether they are more than 1 or not (INERIS, 2008).The results showed that $\sum HI$ values are much less than 1. As a result, it can be concluded that observing adverse threshold effects are insignificant for a child who ingests soil mixed with sludge. However, it is obvious that the results only include one pathway. There are other pathways that a child may be exposed. Therefore, other pathways should also be taken into account for comprehensive evaluation of threshold effects.

As the soil background concentrations and sludge concentrations were compared with each other in terms of contributions to $\sum HI$, it can be seen from Figure 4.8 that for all of the heavy metals, contributions from soil is higher than contributions from sludge. It means that soil has a higher risk for child than sludge due to ingestion.

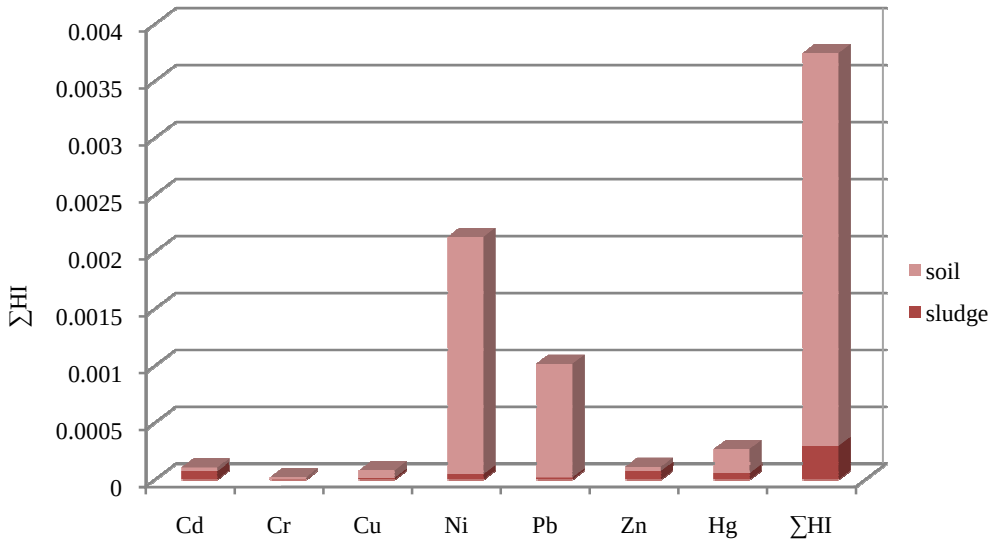

Figure 4.8: Contributions of Background Soil Concentrations (Ankara) and Sludge Concentrations of ACWWTP to $\sum HI$

4.2.2.2. Health Risk Calculations for Non-Threshold (Cancer) Effects

Health risks for non-threshold effects were only calculated for PCBs since there are no TRV values provided in INERIS's study for other pollutants (See Appendix C). The Excess of Risk (ER) values for PCBs calculated for only child ingesting soil mixed with sludge pathway are given in Figure 4.9. In June and July, ER values are higher due to high concentrations of PCBs. However, all results indicate that non-threshold effects due to ingestion of soil mixed with sludge by child are insignificant since all ER values are much less than the acceptable risk level provided by INERIS, which is 10^{-5}.

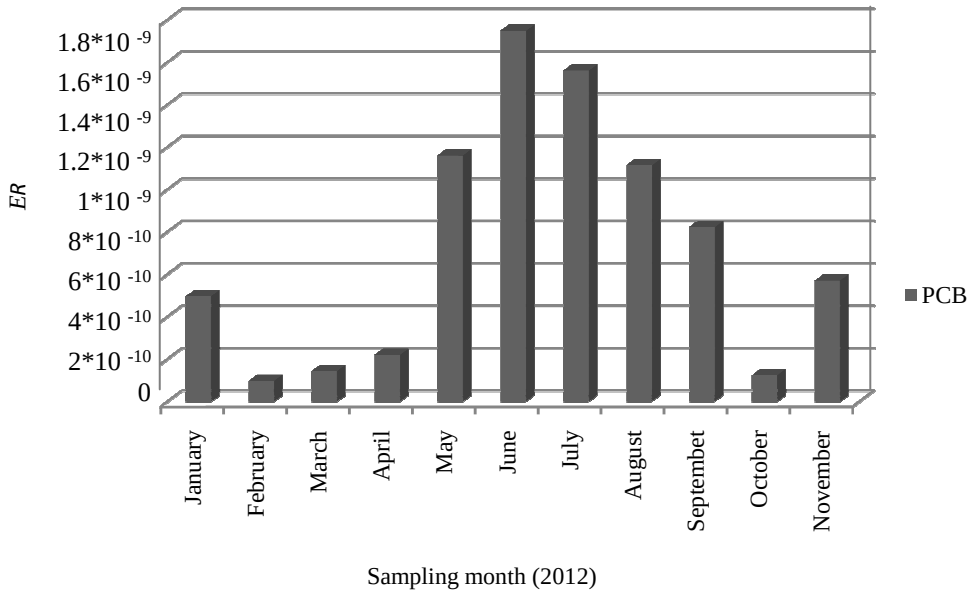

Figure 4.9: Graphical Demonstration of ER for PCB

4.2.2.3. Health Risk Calculations for Limit Values in Turkish Regulation for the Use of Sewage Sludge in Agriculture with INERIS's Method

In this section, sludge limit values included in the Turkish Regulation for the use of sludge in agriculture (2010) were also calculated with INERIS's method in terms of their possible health risks (See Appendix C). Health risks were calculated for both threshold and non-threshold effects for the pollutants which are included within the scope of this study (See Table 3.2) and for just one pathway which is child ingesting soil mixed with sludge (See Section 3.2.2.3). To calculate substance concentrations, the limit values included in the regulation were taken as pollutant concentrations (See Table 2.1). In addition, soil background concentrations were also taken as the soil limit concentrations for heavy metals included in the regulation. It means that soil limit concentrations were summed up with pollutant limit concentrations to determine substance concentrations. In the regulation, there are two types of soil limit concentrations for heavy metals depending on the pH of the soil (See Table 2.3). To be more protective, the highest background soil concentrations standing for pH>7 were chosen for health risk calculations. For organic pollutants, no background concentrations were assumed since there are no soil limit values for these pollutants in the regulation.

For calculation of threshold and non-threshold risks, same steps used in Section 4.2.1.3 were followed and the results are given in Table 4.5. According to the results for threshold effects, highest *HI* belongs to Pb. The main reason for this is Pb has a lower *TRV* value for threshold effects, which makes *HI* value higher. On the other hand, lowest *HI* belongs to NPEs due to lower substance concentration and a high *TRV* value for non-threshold effects. As *HI* values are summed up, $\sum HI$ is found as 0.015 which is a higher value when compared to the $\sum HI$ results of sludge samples of ACWWTP. However, it is much less than 1 which means with the ingestion of soil mixed with sludge pathway, threshold risks are considered to be low for child. It means the limit values for both soil and sludge are protective for child health due to ingestion of soil mixed sludge. However, presence of some other pathways (See Table 2.10) that may be affecting the child must be emphasized again.

Table 4.5: Calculated Parameters for Limit Concentrations in Turkish Regulation for the Use of Sewage Sludge in Agriculture

Heavy Metal	Pollutant Concentrations in Sludge (mg/kg)	Background Soil Concentrations (mg/kg)	Substance Concentrations (mg/kg)	*DED* (mg/kg.day)	*HI*
Cd	10	1.5	2.1	$4.5*10^{-7}$	$4.5*10^{-4}$
Cr	1000	100	164.6	$3.4*10^{-5}$	$2.3*10^{-5}$
Cu	1000	100	164.6	$3.5*10^{-5}$	$2.4*10^{-4}$
Hg	10	1	1.6	$3.5*10^{-7}$	$3.5*10^{-3}$
Ni	300	70	89.3	$1.9*10^{-5}$	$9.4*10^{-4}$
Pb	750	100	148.5	$3.1*10^{-5}$	$8.9*10^{-3}$
Zn	2500	200	361.5	$7.6*10^{-5}$	$2.5*10^{-4}$
PCB	0.8	-	0.06	$1.5*10^{-8}$	$5.4*10^{-4}$
NPE	50	-	0.05	$1.1*10^{-8}$	$2.6*10^{-7}$
				$\sum HI$	**0.015**

If the sludge and soil concentration limit values are compared with each other to see their contributions to $\sum HI$, it is observed that for all selected pollutants, *HI* due to background soil concentration is dominant (Figure 4.10). The main reason for this difference is that sludge concentrations are diluted during spreading to land and concentrations are lowered although cumulative inputs of sludge are taken into consideration. As a result, pollutant concentrations in soil are higher than concentration of pollutants in sludge and the health risks associated with pollutant concentrations in soil is more concerning.

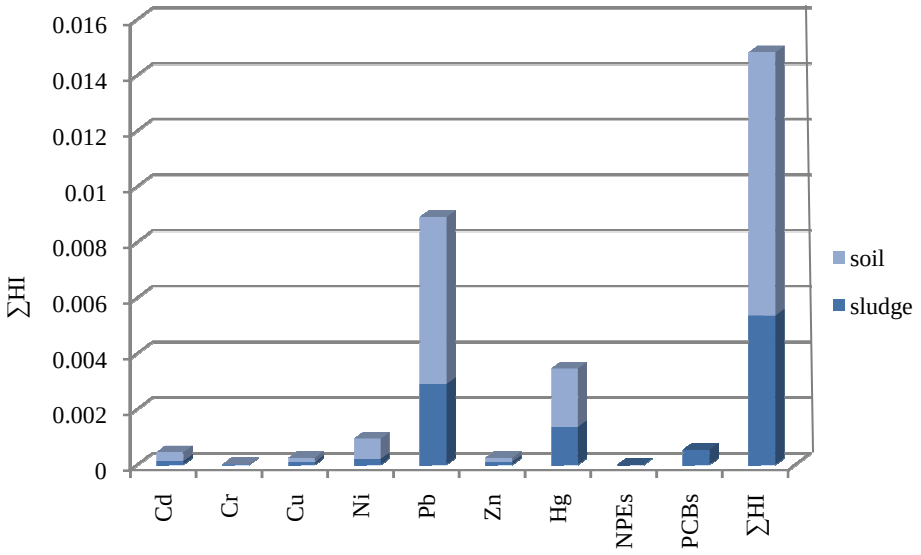

Figure 4.10: Contributions of Background Soil and Sludge Concentrations to $\sum HI$

As stated above, health risk calculations for non-threshold effects were also conducted and the ER value for PCBs is calculated as $2.2*10^{-8}$. According to the results,ER value for PCBs is very low and non-threshold effects are considered to be insignificant for this case since it is three orders of magnitude lower than 10^{-5} which is suggested by INERIS as the acceptable risk level for land spreading of sludge.

4.4. Comparison of the Results of Two U.S. EPA and INERIS's Methods

In this study, two different methods were used for health risk assessment for sludge samples from ACWWTP. According to the results, for both methods, the cancer (non-threshold) and non-cancer (threshold) effects were found to be acceptable for child ingesting biosolids or soil mixed with sludge pathway. However, the results of the U.S. EPA's methods gave higher cumulative non-cancer risk and cancer risk estimates when compared to the results of INERIS's method. It is mainly due to difference in the ingestion of the pollutant source by a child. In the U.S. EPA's method, child ingests 'biosolids' directly from land applied area or biosolids from a bag or a container. Conversely, the pollutant source of the INERIS's method for the selected pathway is 'soil which is mixed with sludge'. For this case, dilution factor and degradation (for only NPEs among the studied chemicals)were taken into account and it resulted in smaller pollutant concentrations in the soil although the application is assumed to happen for 70 years and cumulative inputs were taken into account. The method of U.S. EPA is more protective for human health since worst-case is considered as the type of the pollutant source which is ingested by a child. Other reason that causes different results is that in U.S. EPA's method, for the calculation of non-cancer risks exposure duration adjustment (*DE*) was set to 1 since no approved method is applied by U.S. EPA within the scope of Part 503 Rule to determine *DE* value for children (U.S. EPA, 1992). In the study of INERIS, exposure frequency (F) of child ingesting soil mixed with sludge is assumed in health risk calculations and it lowered the *HI* values calculated.

If non-cancer effects of the pollutants are evaluated for both methodologies, Ni and Cd seem to be the most critical pollutants with the U.S. EPA's method among other heavy metals (Figure 4.4). On the other hand, with INERIS's method, Pb is the most critical pollutant (Figure 4.7). In U.S. EPA's method, *RfD* value was not available for Pb. So, in this study, non-cancer risks could not be calculated for Pb with U.S. EPA's method. In addition, non-cancer risks for NPE and PCB could not be calculated with U.S. EPA's method due to lack of RfD data. As the results of both methodologies are compared, it is observed that non-cancer risks calculated with U.S. EPA's method are more than two orders of magnitude higher than the non-cancer risks calculated with INERIS's method due to differences in these approaches as mentioned above.

Cancer risks were also calculated by both methods for only PCBs. According to the results, cancer risks were lower with INERIS method compared to U.S. EPA's method due to the same reasons mentioned above.

In this study, apart from the determination of health risks for sludge samples of ACWWTP, the sludge and soil limit values in Turkish Regulation for the Use of Sewage Sludge in Agriculture were also used to calculate health risks. In U.S. EPA's method, only sludge limit values were used. On the other hand, in INERIS's method, both soil and sludge limit values were taken into account and summed up to determine substance concentration. According to the results, the cancer risks and non-cancer risks calculated with U.S. EPA's method were much higher than the results of INERIS's method due to the same reasons explained above.

If two methods are compared in general, it is obvious that U.S. EPA's method is more protective than INERIS's method. Although U.S. EPA's method gave higher cancer and non-cancer risk results, the health concerns do not pose a significant risk for only 'child ingesting sludge' pathway.

4.5. Discussion of the Health Risk Assessment Results

For both methods, health risks associated with land application of sludge samples originating from ACWWTP were found to be acceptable for the ingestion of sludge by a child pathway. The results show similar tendencies with other health risk assessment studies found in literature. In the study of INERIS (2008) health risks due to ingestion of sludge and soil mixture by a child was also determined as acceptable and the cumulative health risks were determined as acceptable as well. In the study of VKM (2009), the health risk due to ingestion of soil mixed with sludge by a child was also found to be very low.

In this study, there are some limitations. This study only gives the health risk results due to child ingesting the sludge (or for INERIS approach ingesting the mixture of the sludge and the soil) pathway. There may be additional health risks due to other pathways such as ingestion of animal products and plants and drinking water. However, other pathways were not taken into account and the health risks due to other pathways were not calculated. It should be remembered that child ingesting sludge pathway was identified as the most conservative pathway by U.S. EPA (1995) for 5 heavy metals regulated by Part 503 Rule. In addition, a total of 9 pollutants were considered throughout the study since those were the only compounds that could be analyzed at METU Environmental Engineering Department laboratory. There might be other pollutants which have carcinogenic and/or non-carcinogenic health effects and they may lead to additional health risks for child. These are the uncertainties of this study. In order to reduce the limitations, more comprehensive studies should be conducted.

In this study, health risks due to ingestion of sludge by a child pathway were determined and to be below the acceptable risk values recommended by U.S. EPA (1995) and INERIS (2008).However, other pathways should also be taken into account to determine a cumulative health risk for each receptor. As a result, whether the sludge samples can be used in land application or not requires a more extensive study.

CHAPTER 5

SUMMARY & CONCLUSION

This study is the first study conducted in Turkey concerning health risk assessment for land application of biosolids. All heavy metal concentrations (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) and two of the organic pollutant concentrations (PCBs and NPEs) cited in the current Turkish regulation were examined monthly in sludge samples collected from ACWWTP for the year 2012.Then, health risk assessment methodologies developed by U.S. EPA and INERIS were applied for the samples and both non-cancer and cancer health risks were evaluated. For the calculation of health risks only one pathway (ingestion of sludge by a child) was taken into consideration. The main conclusions that can be driven from the study are as follows.

- The results of heavy metal concentrations and organic pollutant concentrations showed some fluctuations and no particular trend was observed among all concentrations.
    - Cr concentrations ranged between 144 mg/kg and 356.1 mg/kg. In May, June and July (2012), the concentrations were observed to be higher than the other samples.
    - Cu concentrations were measured between 147.1 mg/kg and 230.3 mg/kg. In the first three months of the year (2012), the concentrations were observed to be higher than the other samples.
    - Hg concentrations varied between 0.4 mg/kg and 1.3 mg/kg. In December and November, the Hg concentrations were higher when compared to the results from other months.
    - Ni concentrations were observed between 69.7 mg/kg and 89.9 mg/kg. The highest Ni concentration was observed in May(2012).
    - Pb concentrations were between 35.1 mg/kg and 85.2 mg/kg and a decrease was observed between concentrations from the beginning of the year till the end of the year (2012).
    - Zn concentrations ranged between 1174.7 mg/kg and 2499.9 mg/kg. After August (2012), Zn concentrations were observed to be higher and in November (2012), it reached the highest concentration.
    - PCBs concentrations were observed to be very low and varied between 0.004 mg/kg and 0.06 mg/kg.
    - NPEs concentrations were measured between 5.3 mg/kg and 25.5 mg/kg.
    - All the PCBs, NPEs and heavy metal concentrations except for Zn are much lower than the limit values dictated by the Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010). For land application, most critical pollutantseemed to be Zn. Even though it did not exceed the regulatory limit (2500 mg/kg), in one sample, the concentrationwas as high as the limit value given in the regulation. Therefore, it is recommended that Zn concentrations should be observed attentively before land application.

- *Health Risk Calculations with U.S. EPA's Method for Ingestion of Biosolids by a Child Pathway:*

    - *Non – cancer risks:*The lowest *HI* values were observed for Cr and highest for Ni and Cd, respectively. $\sum HI$ values were calculated to be between 0.16 and 0.25. For all months, the findings suggest that the health risks due to ingestion of biosolids by a child alone due to heavy metals is lowand does not result in adverse non-cancer health effects with respect to acceptable risk levels suggested by EPA and INERIS (U.S. EPA, 1994; INERIS, 2008).

    - *Cancer risks:* The *Risk* values were calculated for PCBs between ?? 10^{-7} and 10^{-8}. When these risks are compared with the acceptable risk level (10^{-4}) which is suggested by U.S. EPA (1995), they are found to be very low. Cancer effects due to PCBsdo not pose a significant risk for child ingesting biosolids pathway.

    - Health risk calculations were conducted for the limit values set in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010):
        - The highest *HI* was observed for Hg limit concentration (10mg/kg) provided in the regulation. The highest $\sum HI$ value was calculated as 0.89 which was very high when compared to the results for sludge samples of ACWWTP. However, since this value is less than 1, non-cancer effects are not considered to be significant for ingestion of biosolids by a child due to seven heavy metals considered in this study. The limit values can be considered as adequately protective for child ingesting biosolids pathway. However, to have a more accurate conclusion, other pathways and receptors should be also taken into account.

        - Risk value for PCB was calculated as $5.5*10^{-6}$. This value is lower than 10^{-4} which is suggested by U.S. EPA (1995) as the acceptable risk level. On the other hand, if acceptable risk level is chosen as 10^{-6}(National Research Council, 2002) and it may become a concern for child's health.

- *Health Risk Calculations with INERIS'S Method for Ingestion of Soil Mixed with Sludge by a Child Pathway:*

    - *Threshold (non-cancer) risks:* Among all pollutants (Cd, Cr, Cu, Hg, Ni, Pb, Zn, PCBs and NPE), Ni had the highest *HI* value. According to $\sum HI$ results, the values varied between 0.0035 and 0.0038 and all the values were lower than 1. Soil concentrations result in higher risks when compared to risk caused by sludge concentrations. However, the results indicated that threshold risks due to selected pollutants are low for child who ingests soil mixed with sludge.

    - *Non-threshold (cancer) risks:* ER values for PCBs were calculated between $9.8*10^{-11}$and $1.7*10^{-9}$. The acceptable level suggested by INERIS (2008) is 10^{-5}. According to results, adverse non-threshold effects due to PCBs would not pose a significant risk for child ingesting soil mixed with sludge.

    - Health risk calculations were also conducted for the limit values provided in Turkish Regulation for the Use of Sewage Sludge in Agriculture (2010):

        - Lowest *HI* was observed for PCBs and highest *HI* was observed for Zn. According to the results, contributions of soil background concentrations to *HI* are much higher when compared to pollutant concentrations (limit values) in sludge.

- $\sum HI$ was calculated summing up all HI values and determined as 0.126. As it is compared with 1, it is very low and developing of threshold effects are considered to be insignificant for a child ingesting soil mixed with sludge. The limit values can be considered as adequately protective for only child ingesting biosolids pathway. However, other pathways and receptors should also be taken into account to give a comprehensive result.

- ER value was calculated as $2.2*10^{-8}$ which is three orders of magnitude lower than the acceptable risk (10^{-5}) suggested by INERIS (2008). The limit value for PCBs is considered to be protective for child health due to ingestion of soil mixed with sludge.

- Both cancer and non-cancer risk estimates were higher with U.S. EPA's method. In general, U.S. EPA's method is more protective than INERIS's method. Different assumptions about pollutant source of the pathway, duration of exposure and exposure frequency are the main reasons causing different results for both methods.

- There are some limitations related to health risks due to other pathways, receptors and other pollutants present in sludge samples in this study. To reduce uncertainties, more comprehensive study should be conducted.

CHAPTER 6

FUTURE WORK

In this study, the health risks associated with land application of biosolids were conducted for only one pathway, which is child ingesting biosolids or soil mixed with sludge, due to limited data. This study is the first work conducted to assess the health risks associated with land application of biosolids. In order to investigate this subject further, some future work can be done as follows.

- It is possible for the child to be exposed to pollutants through other pathways. Health risks for other pathways may also be calculated and summed up to be able to have more accurate total risk estimation results. In addition to child, other human receptors such as adult and ecological receptors such as animals, plants and soil organisms may be also considered to calculate risks due to land application of biosolids.

- Other studies associated with land application of biosolids may also be analyzed in detail to come up with the most appropriate health risk assessment method. For instance, Norway conducted an extensive study for land application of biosolids in 2009. This study may also be evaluated and compared with U.S. EPA and INERIS's studies.

- A number of site-specific data are needed in health risk assessment for land application of biosolids. With limited data it is not possible to evaluate all possible health risks due to land application of biosolids. Required data for calculation of health risks through other pathways and receptors may be gathered or a substructure may be set up in the future.

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APPENDIX A

CARCINOGENICITY OF POLLUTANTS

Table A1. Weight of Evidence Characterization of Pollutants for Carcinogenicity (U.S. EPA, 1986)

Classification Groups	Definition of Groups	Data Availability
Group A	Carcinogenic to humans	Adequate human data (typically epidemiologic data)
Group B1	Probably Carcinogenic to Humans	Sufficient evidence from animal bioassay data, but either limited human evidence
Group B2	Probably Carcinogenic to Humans	Sufficient evidence from animal bioassay data, and little/no human data
Group C	Possibly Carcinogenic to Humans	Limited animal evidence and little or no human data
Group D	Not Classifiable as to Human Carcinogenicity	No adequate data either to support or refute human carcinogenicity
Group E	Evidence of Non-carcinogenicity for Humans	No evidence for carcinogenicity in at least two adequate animal tests in different species/both adequate epidemiologic and animal studies

APPENDIX B

HEALTH RISK CALCULATIONS WITH U.S. EPA'S METHOD

Table B1: Non-Cancer Risk Calculations with U.S. EPA's Methodfor Cd (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	RfD (mg/kg.day)	BW (kg)	HI (unitless)
Cd	January	5.4	0.2	1	1	0.001	16	0.068
	February	6.6	0.2	1	1	0.001	16	0.082
	March	5.6	0.2	1	1	0.001	16	0.070
	April	4.8	0.2	1	1	0.001	16	0.060
	May	2.9	0.2	1	1	0.001	16	0.036
	June	4.2	0.2	1	1	0.001	16	0.053
	July	2.8	0.2	1	1	0.001	16	0.036
	August	3.4	0.2	1	1	0.001	16	0.043
	September	3.7	0.2	1	1	0.001	16	0.046
	October	2.2	0.2	1	1	0.001	16	0.028
	November	5.3	0.2	1	1	0.001	16	0.066
	December	6.9	0.2	1	1	0.001	16	0.087

Table B2: Non-Cancer Risk Calculations with U.S. EPA's Method for Cr (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	RfD (mg/kg.day)	BW (kg)	HI (unitless)
Cr	January	356.2	0.2	1	1	1.5	16	0.003
	February	246.0	0.2	1	1	1.5	16	0.002
	March	252.5	0.2	1	1	1.5	16	0.002
	April	227.7	0.2	1	1	1.5	16	0.002
	May	387.5	0.2	1	1	1.5	16	0.003
	June	378.1	0.2	1	1	1.5	16	0.003
	July	378.9	0.2	1	1	1.5	16	0.003
	August	214.8	0.2	1	1	1.5	16	0.002
	September	145.4	0.2	1	1	1.5	16	0.001
	October	265.1	0.2	1	1	1.5	16	0.002
	November	159.5	0.2	1	1	1.5	16	0.001
	December	143.9	0.2	1	1	1.5	16	0.001

Table B3: Non-Cancer Risk Calculations with U.S. EPA's Method for Cu (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	RfD (mg/kg.day)	BW (kg)	HI (unitless)
Cu	January	230.3	0.2	1	1	0.125	16	0.023
	February	210.9	0.2	1	1	0.125	16	0.021
	March	220.0	0.2	1	1	0.125	16	0.022
	April	147.2	0.2	1	1	0.125	16	0.015
	May	173.1	0.2	1	1	0.125	16	0.017
	June	189.3	0.2	1	1	0.125	16	0.019
	July	181.9	0.2	1	1	0.125	16	0.018
	August	186.2	0.2	1	1	0.125	16	0.019
	September	196.4	0.2	1	1	0.125	16	0.020
	October	177.2	0.2	1	1	0.125	16	0.018
	November	194.6	0.2	1	1	0.125	16	0.019
	December	157.9	0.2	1	1	0.125	16	0.016

Table B4: Non-Cancer Risk Calculations with U.S. EPA's Method for Hg (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	RfD (mg/kg.day)	BW (kg)	HI (unitless)
Hg	January	0.4	0.2	1	1	0.0003	16	0.017
	February	0.5	0.2	1	1	0.0003	16	0.022
	March	0.8	0.2	1	1	0.0003	16	0.034
	April	0.5	0.2	1	1	0.0003	16	0.028
	May	0.9	0.2	1	1	0.0003	16	0.033
	June	1.1	0.2	1	1	0.0003	16	0.046
	July	1.0	0.2	1	1	0.0003	16	0.041
	August	0.7	0.2	1	1	0.0003	16	0.028
	September	0.8	0.2	1	1	0.0003	16	0.033
	October	0.8	0.2	1	1	0.0003	16	0.035
	November	1.3	0.2	1	1	0.0003	16	0.053
	December	1.3	0.2	1	1	0.0003	16	0.055

Table B5: Non-Cancer Risk Calculations with U.S. EPA's Method for Ni (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	RfD (mg/kg.day)	BW (kg)	HI (unitless)
Ni	January	88.7	0.2	1	1	0.02	16	0.055
	February	78.8	0.2	1	1	0.02	16	0.049
	March	77.8	0.2	1	1	0.02	16	0.049
	April	76.7	0.2	1	1	0.02	16	0.048
	May	89.9	0.2	1	1	0.02	16	0.056
	June	80.8	0.2	1	1	0.02	16	0.051
	July	74.7	0.2	1	1	0.02	16	0.047
	August	72.1	0.2	1	1	0.02	16	0.045
	September	79.3	0.2	1	1	0.02	16	0.050
	October	69.7	0.2	1	1	0.02	16	0.044
	November	76.8	0.2	1	1	0.02	16	0.048
	December	75.4	0.2	1	1	0.02	16	0.047

Table B6: Non-Cancer Risk Calculations with U.S. EPA's Method for Zn (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	RfD (mg/kg.day)	BW (kg)	HI (unitless)
Zn	January	1514.2	0.2	1	1	0.625	16	0.03
	February	1390.2	0.2	1	1	0.625	16	0.028
	March	1404.5	0.2	1	1	0.625	16	0.028
	April	1224.2	0.2	1	1	0.625	16	0.024
	May	1174.7	0.2	1	1	0.625	16	0.023
	June	1366.2	0.2	1	1	0.625	16	0.027
	July	1450.9	0.2	1	1	0.625	16	0.029
	August	2133.7	0.2	1	1	0.625	16	0.043
	September	2162.4	0.2	1	1	0.625	16	0.043
	October	1928.7	0.2	1	1	0.625	16	0.039
	November	2499.9	0.2	1	1	0.625	16	0.050
	December	1955.7	0.2	1	1	0.625	16	0.039

Table B7: Cancer Risk Calculations with U.S. EPA's Method for PCB (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Average Concentration (mg/kg)	Is (g/day)	DE (unitless)	RE (unitless)	q_1^* $(mg/kg.day)^{-1}$	BW (kg)	$Risk$ (unitless)
PCB	February	0.018	0.2	0.0714	1	7.7	16	$1.3*10^{-7}$
	March	0.004	0.2	0.0714	1	7.7	16	$2.5*10^{-8}$
	April	0.005	0.2	0.0714	1	7.7	16	$3.6*10^{-8}$
	May	0.008	0.2	0.0714	1	7.7	16	$5.6*10^{-8}$
	June	0.043	0.2	0.0714	1	7.7	16	$2.9*10^{-7}$
	July	0.064	0.2	0.0714	1	7.7	16	$4.4*10^{-7}$
	August	0.057	0.2	0.0714	1	7.7	16	$3.9*10^{-7}$
	September	0.041	0.2	0.0714	1	7.7	16	$2.8*10^{-7}$
	October	0.030	0.2	0.0714	1	7.7	16	$2.1*10^{-7}$
	November	0.005	0.2	0.0714	1	7.7	16	$3.2*10^{-8}$
	December	0.021	0.2	0.0714	1	7.7	16	$1.5*10^{-7}$

Table B8: Non-Cancer Risk Calculations with U.S. EPA's Method
(Pollutant Limit Values in Turkish Regulation for the Use of Sewage Sludge in Agriculture, 2010)

	Limit Value (mg/kg)	**Is (g/day)**	**DE (unitless)**	**RE (unitless)**	$\boldsymbol{RfD}$ **(mg/kg.day)**	**BW (kg)**	$\boldsymbol{HI}$ **(unitless)**
Cd	10	0.2	1	1	0.001	16	0.125
Cr	1000	0.2	1	1	1.5	16	0.008
Cu	1000	0.2	1	1	0.125	16	0.100
Hg	10	0.2	1	1	0.0003	16	0.417
Ni	300	0.2	1	1	-	16	0.188
Pb	750	0.2	1	1	0.02	16	-
Zn	2500	0.2	1	1	0.625	16	0.050

Table B9: Cancer Risk Calculations with U.S. EPA's Method
(Pollutant Limit Values in Turkish Regulation for the Use of Sewage Sludge in Agriculture, 2010)

	Limit Value (mg/kg)	**Is (g/day)**	**DE (unitless)**	**RE (unitless)**	$\boldsymbol{q_1^*}$ **(mg/kg.day)$^{-1}$**	**BW (kg)**	$\boldsymbol{Risk}$ **(unitless)**
PCB	0.8	0.2	0.0714	1	7.7	16	$5.5*10^{-6}$

APPENDIX C

HEALTH RISK CALCULATIONS WITH INERIS'S METHOD

Table C1: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Cd (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Cd	January	0.59	0.0009	150	0.021	15	$1.2*10^{-7}$	0.001	$1.2*10^{-4}$
	February	0.66	0.0009	150	0.021	15	$1.4*10^{-7}$	0.001	$1.4*10^{-4}$
	March	0.60	0.0009	150	0.021	15	$1.2*10^{-7}$	0.001	$1.2*10^{-4}$
	April	0.55	0.0009	150	0.021	15	$1.1*10^{-7}$	0.001	$1.1*10^{-4}$
	May	0.42	0.0009	150	0.021	15	$8.9*10^{-8}$	0.001	$8.9*10^{-5}$
	June	0.51	0.0009	150	0.021	15	$1.1*10^{-7}$	0.001	$1.1*10^{-4}$
	July	0.42	0.0009	150	0.021	15	$8.9*10^{-8}$	0.001	$8.9*10^{-5}$
	August	0.46	0.0009	150	0.021	15	$9.7*10^{-8}$	0.001	$9.7*10^{-5}$
	September	0.48	0.0009	150	0.021	15	$1.1*10^{-7}$	0.001	$1.0*10^{-4}$
	October	0.38	0.0009	150	0.021	15	$8.0*10^{-8}$	0.001	$8.1*10^{-5}$
	November	0.58	0.0009	150	0.021	15	$1.2*10^{-7}$	0.001	$1.2*10^{-4}$
	December	0.69	0.0009	150	0.021	15	$1.4*10^{-7}$	0.001	$1.4*10^{-5}$

Table C2: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Cr (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Cr	January	160.01	0.0009	150	0.021	15	$3.4*10^{-5}$	1.5	$2.2*10^{-5}$
	February	152.89	0.0009	150	0.021	15	$3.2*10^{-5}$	1.5	$2.1*10^{-5}$
	March	153.31	0.0009	150	0.021	15	$3.2*10^{-5}$	1.5	$2.1*10^{-5}$
	April	151.71	0.0009	150	0.021	15	$3.2*10^{-5}$	1.5	$2.1*10^{-5}$
	May	155.58	0.0009	150	0.021	15	$3.2*10^{-5}$	1.5	$2.2*10^{-5}$
	June	161.46	0.0009	150	0.021	15	$3.4*10^{-5}$	1.5	$2.2*10^{-5}$
	July	161.51	0.0009	150	0.021	15	$3.4*10^{-5}$	1.5	$2.2*10^{-5}$
	August	150.79	0.0009	150	0.021	15	$3.2*10^{-5}$	1.5	$2.1*10^{-5}$
	September	146.41	0.0009	150	0.021	15	$3.1*10^{-5}$	1.5	$2.0*10^{-5}$
	October	154.16	0.0009	150	0.021	15	$3.2*10^{-5}$	1.5	$2.2*10^{-5}$
	November	147.24	0.0009	150	0.021	15	$3.1*10^{-5}$	1.5	$2.1*10^{-5}$
	December	146.30	0.0009	150	0.021	15	$3.1*10^{-5}$	1.5	$2.0*10^{-5}$

Table C3: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Cu (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Cu	January	57.38	0.0009	150	0.021	15	$1.2*10^{-5}$	0.14	$8.6*10^{-5}$
	February	56.13	0.0009	150	0.021	15	$1.2*10^{-5}$	0.14	$8.4*10^{-5}$
	March	56.62	0.0009	150	0.021	15	$1.2*10^{-5}$	0.14	$8.5*10^{-5}$
	April	52.01	0.0009	150	0.021	15	$1.1*10^{-5}$	0.14	$7.8*10^{-5}$
	May	53.69	0.0009	150	0.021	15	$1.1*10^{-5}$	0.14	$8.1*10^{-5}$
	June	54.74	0.0009	150	0.021	15	$1.2*10^{-5}$	0.14	$8.2*10^{-5}$
	July	54.27	0.0009	150	0.021	15	$1.1*10^{-5}$	0.14	$8.1*10^{-5}$
	August	54.51	0.0009	150	0.021	15	$1.1*10^{-5}$	0.14	$8.2*10^{-5}$
	September	55.21	0.0009	150	0.021	15	$1.2*10^{-5}$	0.14	$8.3*10^{-5}$
	October	53.94	0.0009	150	0.021	15	$1.1*10^{-5}$	0.14	$8.1*10^{-5}$
	November	55.09	0.0009	150	0.021	15	$1.2*10^{-5}$	0.14	$8.3*10^{-5}$
	December	52.71	0.0009	150	0.021	15	$1.1*10^{-5}$	0.14	$7.9*10^{-5}$

Table C4: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Hg (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Hg	January	0.11	0.0009	150	0.021	15	$2.2*10^{-8}$	0.0001	$2.2*10^{-4}$
	February	0.11	0.0009	150	0.021	15	$2.5*10^{-8}$	0.0001	$2.5*10^{-4}$
	March	0.13	0.0009	150	0.021	15	$2.8*10^{-8}$	0.0001	$2.8*10^{-4}$
	April	0.12	0.0009	150	0.021	15	$2.5*10^{-8}$	0.0001	$2.5*10^{-4}$
	May	0.14	0.0009	150	0.021	15	$2.9*10^{-8}$	0.0001	$2.9*10^{-4}$
	June	0.15	0.0009	150	0.021	15	$3.2*10^{-8}$	0.0001	$3.2*10^{-4}$
	July	0.14	0.0009	150	0.021	15	$3.0*10^{-8}$	0.0001	$3.0*10^{-4}$
	August	0.12	0.0009	150	0.021	15	$2.6*10^{-8}$	0.0001	$2.6*10^{-4}$
	September	0.13	0.0009	150	0.021	15	$2.7*10^{-8}$	0.0001	$2.7*10^{-4}$
	October	0.13	0.0009	150	0.021	15	$2.8*10^{-8}$	0.0001	$2.8*10^{-4}$
	November	0.16	0.0009	150	0.021	15	$3.4*10^{-8}$	0.0001	$3.4*10^{-4}$
	December	0.17	0.0009	150	0.021	15	$3.5*10^{-8}$	0.0001	$3.5*10^{-4}$

Table C5: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Ni (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Ni	January	203.73	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	February	203.09	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	March	203.03	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	April	202.95	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	May	203.80	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	June	203.23	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	July	203.11	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	August	202.65	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	September	203.13	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	October	203.49	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	November	202.97	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$
	December	202.97	0.0009	150	0.021	15	$4.3*10^{-5}$	0.0001	$2.1*10^{-4}$

Table C6: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Pb (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Pb	January	17.86	0.0009	150	0.021	15	$3.8*10^{-6}$	0.0035	$1.1*10^{-3}$
	February	18.11	0.0009	150	0.021	15	$3.8*10^{-6}$	0.0035	$1.1*10^{-3}$
	March	18.51	0.0009	150	0.021	15	$3.9*10^{-6}$	0.0035	$1.1*10^{-3}$
	April	17.99	0.0009	150	0.021	15	$3.6*10^{-6}$	0.0035	$1.0*10^{-3}$
	May	16.84	0.0009	150	0.021	15	$3.5*10^{-6}$	0.0035	$1.0*10^{-3}$
	June	17.24	0.0009	150	0.021	15	$3.6*10^{-6}$	0.0035	$1.0*10^{-3}$
	July	17.65	0.0009	150	0.021	15	$3.7*10^{-6}$	0.0035	$1.1*10^{-3}$
	August	16.73	0.0009	150	0.021	15	$3.5*10^{-6}$	0.0035	$1.0*10^{-3}$
	September	16.36	0.0009	150	0.021	15	$3.4*10^{-6}$	0.0035	$9.8*10^{-4}$
	October	16.40	0.0009	150	0.021	15	$3.5*10^{-6}$	0.0035	$9.9*10^{-4}$
	November	15.26	0.0009	150	0.021	15	$3.2*10^{-6}$	0.0035	$9.2*10^{-4}$
	December	15.30	0.0009	150	0.021	15	$3.2*10^{-6}$	0.0035	$9.2*10^{-4}$

Table C7: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for Zn (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
Zn	January	151.9	0.0009	150	0.021	15	$3.9*10^{-5}$	0.3	$1.1*10^{-4}$
	February	143.9	0.0009	150	0.021	15	$3.0*10^{-5}$	0.3	$1.0*10^{-4}$
	March	144.8	0.0009	150	0.021	15	$3.0*10^{-5}$	0.3	$1.0*10^{-4}$
	April	133.2	0.0009	150	0.021	15	$2.8*10^{-5}$	0.3	$9.3*10^{-5}$
	May	130.0	0.0009	150	0.021	15	$2.7*10^{-5}$	0.3	$9.1*10^{-5}$
	June	142.5	0.0009	150	0.021	15	$2.9*10^{-5}$	0.3	$9.9*10^{-5}$
	July	147.5	0.0009	150	0.021	15	$3.1*10^{-5}$	0.3	$1.0*10^{-4}$
	August	191.6	0.0009	150	0.021	15	$4.0*10^{-5}$	0.3	$1.3*10^{-4}$
	September	194.1	0.0009	150	0.021	15	$4.1*10^{-5}$	0.3	$1.4*10^{-4}$
	October	178.5	0.0009	150	0.021	15	$3.7*10^{-5}$	0.3	$1.2*10^{-4}$
	November	215.6	0.0009	150	0.021	15	$4.5*10^{-5}$	0.3	$1.5*10^{-4}$
	December	180.5	0.0009	150	0.021	15	$3.8*10^{-5}$	0.3	$1.2*10^{-4}$

Table C8: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for PCB (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV(for threshold)	HI
PCB	January	-	0.0009	150	0.021	15	-	0.0002	-
	February	0.0011	0.0009	150	0.021	15	$2.5*10^{-10}$	0.0002	$1.2*10^{-5}$
	March	0.0002	0.0009	150	0.021	15	$4.9*10^{-11}$	0.0002	$2.4*10^{-6}$
	April	0.0003	0.0009	150	0.021	15	$7.2*10^{-11}$	0.0002	$3.6*10^{-6}$
	May	0.0005	0.0009	150	0.021	15	$1.1*10^{-10}$	0.0002	$5.5*10^{-6}$
	June	0.0027	0.0009	150	0.021	15	$5.8*10^{-10}$	0.0002	$2.9*10^{-5}$
	July	0.0040	0.0009	150	0.021	15	$8.7*10^{-10}$	0.0002	$4.4*10^{-5}$
	August	0.0037	0.0009	150	0.021	15	$7.8*10^{-10}$	0.0002	$3.9*10^{-5}$
	September	0.0026	0.0009	150	0.021	15	$5.6*10^{-10}$	0.0002	$2.8*10^{-5}$
	October	0.0019	0.0009	150	0.021	15	$4.1*10^{-10}$	0.0002	$2.1*10^{-5}$
	November	0.0003	0.0009	150	0.021	15	$6.2*10^{-11}$	0.0002	$3.1*10^{-6}$
	December	0.0013	0.0009	150	0.021	15	$2.8*10^{-10}$	0.0002	$1.4*10^{-5}$

Table C9: Threshold (Non-Cancer) Risk Calculations with INERIS's Method for NPE (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV (for threshold)	HI
NPE	January	-	0.0009	150	0.021	15	-	0.045	-
	February	0.0077	0.0009	150	0.021	15	$1.6*10^{-9}$	0.045	$3.6*10^{-8}$
	March	0.0080	0.0009	150	0.021	15	$1.7*10^{-9}$	0.045	$3.7*10^{-8}$
	April	0.0086	0.0009	150	0.021	15	$1.8*10^{-9}$	0.045	$4.0*10^{-8}$
	May	0.0096	0.0009	150	0.021	15	$2.0*10^{-9}$	0.045	$4.5*10^{-8}$
	June	0.0096	0.0009	150	0.021	15	$2.0*10^{-9}$	0.045	$4.5*10^{-8}$
	July	0.0136	0.0009	150	0.021	15	$2.9*10^{-9}$	0.045	$6.4*10^{-8}$
	August	0.0219	0.0009	150	0.021	15	$4.4*10^{-9}$	0.045	$9.8*10^{-8}$
	September	0.0097	0.0009	150	0.021	15	$2.0*10^{-9}$	0.045	$45*10^{-8}$
	October	0.0097	0.0009	150	0.021	15	$2.0*10^{-9}$	0.045	$4.5*10^{-8}$
	November	0.0114	0.0009	150	0.021	15	$2.4*10^{-9}$	0.045	$5.3*10^{-8}$
	December	0.0096	0.0009	150	0.021	15	$2.0*10^{-9}$	0.045	$4.5*10^{-8}$

Table C10: Non-Threshold (Cancer) Risk Calculations with INERIS's Method (Sludge Samples of ACWWTP)

	Sampling Month (2012)	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV (for non-threshold)	ER
PCB	January		0.0009	150	0.021	15	-	2	-
	February	0.0011	0.0009	150	0.021	15	$2.5*10^{-10}$	2	$4.9*10^{-10}$
	March	0.0002	0.0009	150	0.021	15	$4.9*10^{-11}$	2	$9.8*10^{-11}$
	April	0.0003	0.0009	150	0.021	15	$7.2*10^{-11}$	2	$1.4*10^{-10}$
	May	0.0005	0.0009	150	0.021	15	$1.1*10^{-10}$	2	$2.2*10^{-10}$
	June	0.0027	0.0009	150	0.021	15	$5.8*10^{-10}$	2	$1.2*10^{-9}$
	July	0.0040	0.0009	150	0.021	15	$8.7*10^{-10}$	2	$1.7*10^{-9}$
	August	0.0037	0.0009	150	0.021	15	$7.8*10^{-10}$	2	$1.6*10^{-9}$
	September	0.0026	0.0009	150	0.021	15	$5.6*10^{-10}$	2	$1.1*10^{-9}$
	October	0.0019	0.0009	150	0.021	15	$4.1*10^{-10}$	2	$8.2*10^{-10}$
	November	0.0003	0.0009	150	0.021	15	$6.2*10^{-11}$	2	$1.2*10^{-10}$
	December	0.0013	0.0009	150	0.021	15	$2.8*10^{-10}$	2	$5.7*10^{-10}$

Table C11: Threshold (Non-Cancer) Risk Calculations with INERIS's Method
(Pollutant Limit Values in Turkish Regulation for the Use of Sewage Sludge in Agriculture, 2010)

	Substance Concentration (mg/kg)	DF (unitless)	$M_{ingested\ soil}$ (mg/day)	F (unitless)	BW (kg)	DED	TRV (for threshold)	HI
Cd	2.1	0.0009	150	0.021	15	$4.5*10^{-7}$	0.001	$4.5*10^{-4}$
Cr	164.6	0.0009	150	0.021	15	$3.4*10^{-5}$	1.5	$2.3*10^{-5}$
Cu	164.6	0.0009	150	0.021	15	$3.5*10^{-5}$	0.14	$2.4*10^{-4}$
Hg	1.6	0.0009	150	0.021	15	$3.5*10^{-7}$	0.0001	$3.5*10^{-3}$
Ni	89.3	0.0009	150	0.021	15	$1.9*10^{-5}$	0.02	$9.4*10^{-4}$
Pb	148.5	0.0009	150	0.021	15	$3.1*10^{-5}$	0.0035	$8.9*10^{-3}$
Zn	361.5	0.0009	150	0.021	15	$7.6*10^{-5}$	0.3	$2.5*10^{-4}$
PCB	0.06	0.0009	150	0.021	15	$1.5*10^{-8}$	0.0002	$5.4*10^{-4}$
NPE	0.05	0.0009	150	0.021	15	$1.1*10^{-8}$	0.045	$2.6*10^{-7}$

Table C12: Non-Threshold (Cancer) Risk Calculations with INERIS's Method
(Pollutant Limit Values in Turkish Regulation for the Use of Sewage Sludge in Agriculture, 2010)

	Substance Concentration (mg/kg)	**DF (unitless)**	**$M_{ingested\ soil}$ (mg/day)**	**F (unitless)**	**BW (kg)**	**DED**	**TRV (for non-threshold)**	**ER**
PCB	0.051	0.0009	150	0.021	15	$1.1*10^{*8}$	2	$2.2*10^{-8}$