SAKARYA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ

Sakarya University Journal of Science
SAUJS

e-ISSN 2147-835X Period Bimonthly Founded 1997 Publisher Sakarya University
http://www.saujs.sakarya.edu.tr/

Title: Sustainable Remediation of Atrazine in Agricultural Fields by Reusing Contaminated Water for Irrigation

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Recieved: 2021-06-20 00:00:00

Accepted: 2021-12-28 00:00:00

Article Type: Research Article

Volume: 26
Issue: 1
Month: February
Year: 2022
Pages: 136-148

How to cite
Zohre KURT; (2022), Sustainable Remediation of Atrazine in Agricultural Fields by Reusing Contaminated Water for Irrigation. Sakarya University Journal of Science, 26(1), 136-148, DOI: 10.16984/saufenbilder.955012
Access link
http://www.saujs.sakarya.edu.tr/tr/pub/issue/67934/955012

Sakarya University Journal of Science 26(1), 136-148, 2022

Sustainable Remediation of Atrazine in Agricultural Fields by Reusing Contaminated Water for Irrigation

Zohre KURT*[1]

Abstract

High yields of agricultural produce is reached traditionally by the application of fertilizers and/or pesticides. When agricultural soil is saturated with pesticides, any pesticide addition to the soil leaches and thus reaches the underlying groundwater. Preventing further contamination and remediation of this type of contamination remains to be a challenge. Although monitored natural attenuation has been shown as an ultimate solution for decontamination, additional applications have been introduced to rapidly achieve this goal. One solution that also contains economic benefits to the farmers is to pump and reuse. The study described here evaluates the possibility to use pump and reuse technique for atrazine. In this study, six field samples have been evaluated for their atrazine biodegradation capacity. By placing them in sterilized controls and inoculated active columns, field conditions are replicated to study the leaching and biodegradation at the topsoil of agricultural fields. The biodegradation capacities of inoculated active columns ranged between 34 and 75 mg/kg/day of atrazine. The results indicated that using the contaminated water for irrigation could eliminate the pesticide contamination from the soil and groundwater. Overall, this method provides a sustainable solution for pesticide use and remediation by minimizing the pesticide use in agricultural fields without affecting the yield of the planted crops.

Keywords: Biodegradation, pesticide, atrazine, sustainable treatment, pump and treat

1. INTRODUCTION

Pesticide application is inevitable when high yield of the crops is desired. Most of the recommended pesticide amounts overdose the soil and cause contamination that not only stays in the soil but also leaches to the underlying groundwater [1-3]. Since groundwater is a source for agricultural irrigation, contamination prevents its use or requires expensive treatment methodologies [4, 5]. One way to treat the contaminated groundwater is through microbial activities. Biodegradation of pesticides in the soil has been studied extensively and when sufficient organisms, water, and electron acceptor were present it was shown that the soil is effectively decontaminated [6-9]. However, studies of biodegradation of pesticides in the groundwater have shown that microbial activity for the natural attenuation is slow and therefore the groundwater contamination can persist.

With the scarcity of clean water resources, new technologies and methodologies need to be

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developed to save and clean the currently available resources. Pump and treat, biostimulation and bioaugmentation are methodologies that can be used to decontaminate the groundwater. Recently, a pump and reuse technique that uses contaminated groundwater for irrigation has been described where contaminated groundwater to remove nitrate from the groundwater was modeled and showed that decontamination of groundwater can be achieved while using the contaminant (nitrate) as a resource (in this case a fertilizer) [10]. The model showed that pump and treat could provide a sustainable treatment of the groundwater whereas reducing the fertilizer expenses for the farmers. However, the study did not include any experimental data showing that the model could actually work in field conditions and also could not provide any data for the microbial potential for bioremediation.

The present study proposes that pesticide contaminated water can also be used in agricultural lands to remediate the contamination in the field while reducing pesticide use. Atrazine extensively used in the field, were selected to test this hypothesis. Therefore, soil samples were collected and analyzed for their physical properties and columns representing the topsoil of the agricultural fields were operated in the lab to observe how the pump and treat technique would work in the field.

Atrazine is an a trizine herbicide found in many water bodies [11-13]. Its excessive use result in its appearance in the rivers and groundwater in many countries [14-17]. Although banned in the European Union, atrazine is still used extensively in maize weed controls in the USA [18], , the largest producer of corn in the world [19]. The excessive use of atrazine leads to groundwater contamination with concentrations reaching up to 90 μg/L [20]. Therefore, its bioremediation is an important act that needs to be evaluated. In this study not only its bioremediation but its reutilization has been evaluated.

One way to indicate the biodegradability is to study contaminated soils. Hence, soil samples were collected from different parts suspected with atrazine contamination for this study. Samples analyzed in this study showed that microbial activity was ubiquitous for atrazine. Field columns were designed and operated to mimic the topsoil in the field to evaluate the biodegradation capacities. Operating the field sample columns also revealed that biodegradation capacities of 34 to 75 mg/kg/day for atrazine.

The study described here demonstrates that the novel idea of using contaminated water for irrigation instead of on-site treatment could provide a sustainable treatment option. The findings were further verified using HYDRUS-1D simulations. The overall results indicate that degradation in the topsoil is sufficient to prevent contamination of the groundwater underlying the agricultural field area whereas the adsorption and desorption in the soil provides pesticides concentration sufficient for the crops to grow with desired yield.

2. MATERIALS AND METHODS

2.1. Materials

Atrazine (> 99.5 %), acetonitrile (> 99.9 %), di-sodium phosphate (> 99.5 %) and mono-sodium phosphate (> 99.5 %) were bought from Sigma-Aldrich, USA. Clay was from Milipore Sigma, sand (fine laboratory grade) was from Fisher Scientific and silt (as silt loam) was from AGCLASROOMSTORE .

2.2. Analytical methods

Detection of atrazine was accomplished using high-pressure liquid chromatography (HPLC) for liquid and soil or sediment samples. Liquid samples were centrifuged for 1 min at 3000 rpm prior to analysis, whereas soil and sediment samples were extracted with 50:50 acetonitrile water mixture by vortexing for 3 minutes and letting it sit for 12 hours, then the supernatant was centrifuged for 1 min at 3000 rpm prior to HPLC analysis. Atrazine was analyzed with an isocratic method where Merck reverse phase C18 Chromolith column (100 mm, diameter 4.6 mm) was used with an Agilent 1260 HPLC with a flow rate of 0.5 ml/hr and injection volume of 40 μL. The atrazine was analyzed at 220 nm where the

minimum detection limits were 0.01 μg/L. The minimum detection limits were established based on the minimum concentration that could provide a measurable concentration through HPLC.

2.3. Field samples

The field soil samples were collected from agricultural soils known to be exposed to atrazine (date of application and concentrations not known) that were actively used for maize production in the Amasya, Balikesir and Denizli provinces of Turkey. The samples were analyzed for their atrazine concentrations, moisture content and porosity prior to microcosm or column preparation. Clay, silt, sand and the soil samples were dried in an oven preheated to 105°C for 12 hours before measuring porosity and amount of contaminants. The porosity was estimated by adding known amount of water to the oven dried sample and the moisture content was determined by weighing the sample before and after being placed in the oven. The samples were then classified according to their particle size based on their sand, silt and clay contents after drying [21]. Maximum adsorption capacities of the samples were determined by measuring atrazine concentrations after different quantities of soil was incubated with atrazine initially on their solubility levels. The methodology was developed with the soil quantity that did not have a final concentration of zero at the equilibrium. Briefly, 50 ml of distilled water containing 5 mg/L of atrazine was mixed with 1 g of dry soil, and the concentration of the mixture was measured before and 24 hours after adding the soil. Maximum desorption capacity of every soil sample was determined by filtering the soil after the adsorption tests, mixing 50 ml of distilled water with filtered soil samples, incubating the mixtures for 24 hours and measuring the released contaminant concentration to the distilled water via HPLC. All chemical and physio chemical analyses were performed in triplicates.

2.4. Microcosm

Microcosms were prepared in 50-ml bottles with 5 grams of dry soil and 20 ml of 20 mM phosphate buffer at pH 7.4 and were sealed with Teflon lids. The microcosms were constructed sacrificially in duplicates, and they were incubated at room temperature between 21 and 25°C.

Atrazine was added to the bottles from stock solutions with concentrations of 12.5 mg atrazine/L, and microcosms were vortexed for 1 minute and placed in a shaker at 180 rpm. Controls were prepared with autoclaved soil that also contained the pesticides. The contaminant degradation was monitored by HPLC when a microcosm bottle as sacrificed and extracted for the analysis as described in the analytical methods.

2.5. Enrichments for column incubation

Enrichments were performed to validate the presence of degraders and to obtain a mixed culture for inoculating the columns that will determine the biodegradation potential of every soil. The results from the experiments in this study were used to estimate the amount of atrazine that could be reduced or reused for each agricultural soil type.

In order to prepare 0.1 diluted enrichments both for atrazine in Erlenmeyer flasks, the enrichments obtained after the final microcosm bottles were used. In every dilution, the contaminant concentrations were monitored until complete dissipation before additional 0.1 dilution was performed. The concentrations of the contaminants were measured by taking 1 ml samples from the Erlenmeyer flasks and extracting it with the sediment extraction procedure mentioned in the analytical methods. Final cultures used for the column studies were obtained after the overall 0.001 dilution of the original microcosm sample was reached.

2.6. Column Studies

Glass columns with 25 cm of height and 2.2 cm diameter were designed to mimic drip irrigation with flow rate of 60 ml/hr. similar to average solar dripper flow [22]. The pumped water was saturated with oxygen and contained either 10 mg atrazine/L, representing the concentration of the pesticide dissolved in water in the field. In order

to contain the filling material, the column contained stainless steel mesh on both ends with the size of 20 microns. Both ends of the column also contained sterile filters to prevent any external biological contamination (Figure 1). In order to determine the leaching and aerobic degradation capacity of atrazine in the topsoil in an agricultural field, the column was filled with sand and silt or soil samples from the field up to 15 cm of height. The sand, silt and clay content of the field soil are provided in Table 1. Clay was not used in the column because of its poor infiltration capacity.

The sterile columns were prepared with the column materials mentioned above and autoclaved 3 times for 2 hours each at 121°C under 15 psi. The active columns were prepared with the field samples and were inoculated by adding 10 ml of either atrazine enriched cultures described in the microcosm method above. The enrichments containing either atrazine degraders had optical densities between 0.2 and 0.4 at 600 nm. The contaminant concentrations were monitored via HPLC for influent and effluent of the columns.

2.7. Model Simulation

Model simulation was carried out using HYDRUS-1D package [23] for a soil column having a diameter of 1.1 cm with an active layer of 15 cm representing the topsoil. The entire modeled column was assumed to be 3 m deep representing a shallow vadose zone. The topsoil was assumed to be utilized for cultivation of corn, and the water uptake parameters of corn were taken from Hatipoğlu and Kurt (2019) and the water requirement of the corn was found using Criwar 3.0 based on the generic climate values of corn grown areas in Turkey [24]. The time frame for the corn growth was assumed to be from May to August. Based on the Criwar output data, the irrigation water requirement for the corn was considered as 290, 920, 2110 and 1815 m^3/ha for the months May, June, July and August, respectively. Similarly, the crop evapotranspiration and coefficient were estimated for time period from May to August as 58, 117, 223 and 190 mm, and 0.41, 0.70, 1.06 and 1.04, respectively.

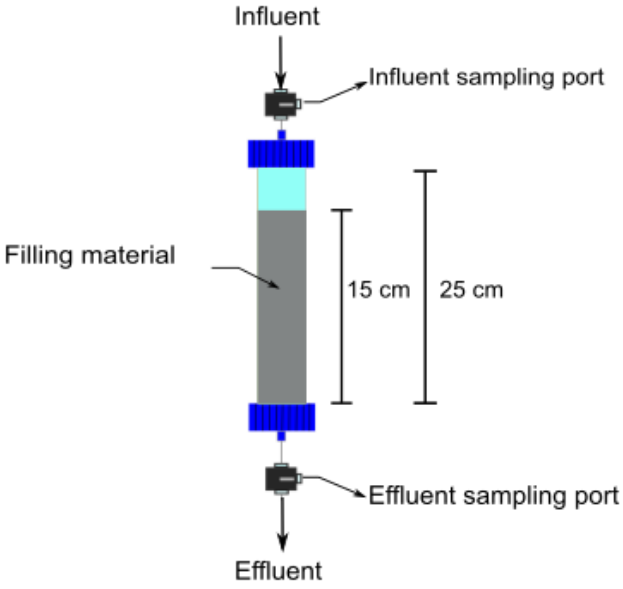

Figure 1 Schematic diagram of the column filled with sand, silt or field soil

Adsorption, desorption and biodegradation parameters were determined based on the field sample analyses conducted as part of this study. The pesticide concentration was kept at the solubility levels of the pesticides in water when introduced to the system, and the rest of the water was assumed to be contamination free. The two scenarios that were constructed to represent drip irrigation were conducted with flow rates of 60 ml/hr and 2 l/hr. representing the average solar drip systems and average conventional drip irrigation systems, respectively. Control scenarios were constructed without any biodegradation. The total amount of the atrazine application was assumed to be 2.5 pound/acre (0.1 mg / column modeled) representing the maximum allowed quantity [18]. The rest of the parameters were kept as default within HYDRUS 1-D.

3. RESULTS AND DISCUSSIONS

3.1. Estimating field sample characteristics

The soil samples collected for the study were characterized according to their silt, clay and sand

content after being autoclaved and dried (Table 1). The results showed that the majority of the soils were classified as loam based on the ternary diagram [25], indicating that the ratio of silt, clay and sand provides a good soil structure that is suitable for agricultural activities [26]. Measured soil properties are consistent with the sampling areas that are actively used for commercial agriculture. The measured sorption and desorption capacities for atrazine were similar to the previously obtained adsorption and desorption isotherms of atrazine with agricultural soil [27]. The desorption of atrazine was lower than its adsorption, because the atrazine was bonded with the soil particles as reported before [28]. The findings were consistent with chemical properties of atrazine with Log K_{ow} (5.8) value. Desorption of the contaminant showed that the leaching potential of atrazine was high, which is consistent with the high water solubility of atrazine (33 mg/L).

The soil samples were further analyzed for their porosity, moisture content and contamination levels (Table 2). The porosity levels of the soils were consistent with loamy soil [26]. Moisture content, on the other hand, could change easily with the irrigation habits or meteorological activity in the field, therefore cannot be compared to a reference value. Atrazine was detected in some samples. The results indicated that atrazine had been actively used in the field where samples were collected.

Table 1 Soil grain size distribution and sorption properties of sterile soil samples for atrazine collected from different fields. Analyses were performed in triplicates.

	Sand (%)	Clay (%)	Silt (%)	Maximum adsorption (mg /kg)	Maximum desorption (mg /kg)
Denizli-1	25 ± 2	17 ± 3	49 ± 7	22.7 ± 1.2	15.1 ± 0.2
Denizli-2	28 ± 3	23 ± 2	46 ± 9	19.1 ± 2.4	17.6 ± 1.2
Balikesir-1	31 ± 2	15 ± 4	51 ± 6	11.9 ± 1.1	9.3 ± 0.4
Balikesir-2	21 ± 1	28 ± 3	43 ± 8	25.9 ± 2.9	22.8 ± 0.4
Amasya-1	38 ± 4	16 ± 1	41 ± 10	20.1 ± 0.9	17.9 ± 1.8
Amasya-2	19 ± 1	24 ± 5	58 ± 12	9.2 ± 3.1	5.9 ± 0.3

3.2. Estimating biodegradation rates of field samples

Presence of active organisms that could degrade contaminants is strongly correlated with the detectable contaminant concentrations in the field [29]. Although not all samples contained atrazine as contaminant, microcosms were prepared for all samples (Figures 2) to investigate the possible biodegradation in the field. To develop a representative scenario, the concentrations were selected to be similar to the field concentrations that would be observed after 50 mg/kg of atrazine application [16, 30]. Not every soil sample contained atrazine (Table 2) but all the soil samples contained organisms that could biodegrade atrazine (Figure 2). The observation that all the soils were able to degrade atrazine was consistent with the previous findings that atrazine degraders are ubiquitous [31, 32]. High copy numbers of atrazine catabolic pathway genes are present in the genomes of the atrazine degraders that protects the bacteria from the loss of atrazine catabolic function [33]. In this study, not detecting atrazine but measuring biodegradation also suggested that atrazine degraders do not lose the ability to degrade atrazine even if they were starved.

Table 2 Contamination levels, porosity and moisture content of the soil samples collected. Analyses were performed in triplicates.

	Atrazine (mg/kg)	Porosity (% v/v)	Moisture content (% v/v)
Denzili-1	0.039 ± 0.0091	41 ± 5	17 ± 3
Denizli-2	0.0191 ± 0.0012	36 ± 4	26 ± 2
Balikesir-1	0.006 ± 0.0003	47 ± 2	21 ± 4
Balikesir-2	0.222 ± 0.0034	39 ± 5	18 ± 1
Amasya-1	ND*	33 ± 7	28 ± 3
Amasya-2	ND	48 ± 8	35 ± 2

*ND indicates that the pesticide of interest was not detected in the soil sample.

The biodegradation of atrazine was established by many different species of bacteria and it was found that governing biodegradation pathways are aerobic [34, 35]. The biodegradation in the field was found to follow first order kinetics [36]. Hence, the initial slopes of the concentrations in Figures 2 was used to estimate the biodegradation rates (Table 3). Controls (i.e., red lines) did not show any biodegradation, indicating that the

biodegradation was due to microbial activity rather than an abiotic process.

The biodegradability of atrazine in the field was previously reported and parameters as previous pesticide applications, additional contaminants, pH and time of sampling were reported to affect the biodegradation rates. The microbial atrazine degradation rates in different soil samples collected from the field ranged between 0.06-15 mg/kg/day [37-41]. The reported biodegradation rates in this study were within the range for atrazine.

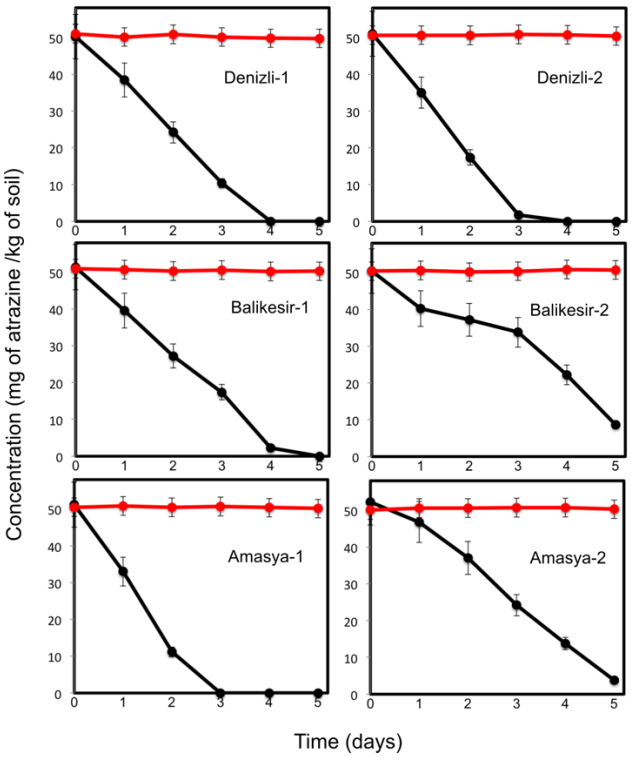

Figure 2 Atrazine concentrations (mg of atrazine/kg of soil) in the microcosms for every soil sample (black). Controls where samples were autoclaved, and atrazine is added (red). All the samples were prepared and measured in duplicates and error bars are the standard deviation between the measurements.

Enrichments were performed using the microcosm samples that showed biodegradation. The samples were diluted with 0.1 increments and monitored for the pesticide degradation until the dilution reached 0.0001. Every sample showing initial biodegradation was successfully enriched assuring that the biodegradation observed is not abiotic and that the degraders were present in the soil samples used for enrichments.

Table 3 Biodegradation rates of the soil samples for atrazine (mg/kg/day)

	Denizli-1	Denizli-2	Balikesir-1	Balikesir-2	Amasya-1	Amasya-2
Atrazine	12.4 ± 0.6	16.4 ± 0.4	12.0 ± 0.2	8.4 ± 1.8	19.1 ± 0.9	6.5 ± 1.1

The biodegradation rates were similar for all samples in terms of atrazine. Although the initial pesticide application to the field samples was not known, measurements of similar rates suggested that the microbial presences of atrazine degraders are similar in samples where biodegradation was observed. Similarly, those results indicated that differences in soil parameters, abiotic degradation, sampling time and leaching are the reasons of the variation of the initial concentrations measured (Table 2) as it was observed for other types of pesticides [41, 42].

3.3. Estimating biodegradation capacity in the topsoil

Columns were designed to mimic the topsoil in the field. Sterilized columns were operated abiotically until they reached steady state or until the influent and effluent concentrations were the same for both atrazine (Figure 3). All the columns reached steady state in less than 5 days. Operating the columns with higher flow rate than 60 ml/hr (100 ml/hr) was not physically possible. Only sterile columns were suitable to determine the adsorbed amounts of the contaminants to the soil because the biodegradation was eliminated. The adsorbed amount of pesticides that was calculated for the columns were between 4.8 and 14.1 mg/kg for atrazine. This quantity was calculated using the amount of influent passing through the column, multiplied by the concentration difference between influent and effluent data divided by the weight of the soil placed in the column (121-152 g). Comparison of the adsorbed amounts of pesticides in the column with the field sample analyses (Table 1) showed that only the field sample analysis provides a close estimate of the maximum adsorption of pesticides in the soil. The slightly lower adsorption in the column was due to the shorter contact time of the contaminant with the soil particles and the channeling effect that might have been observed in a column as also stated in the literature [43].

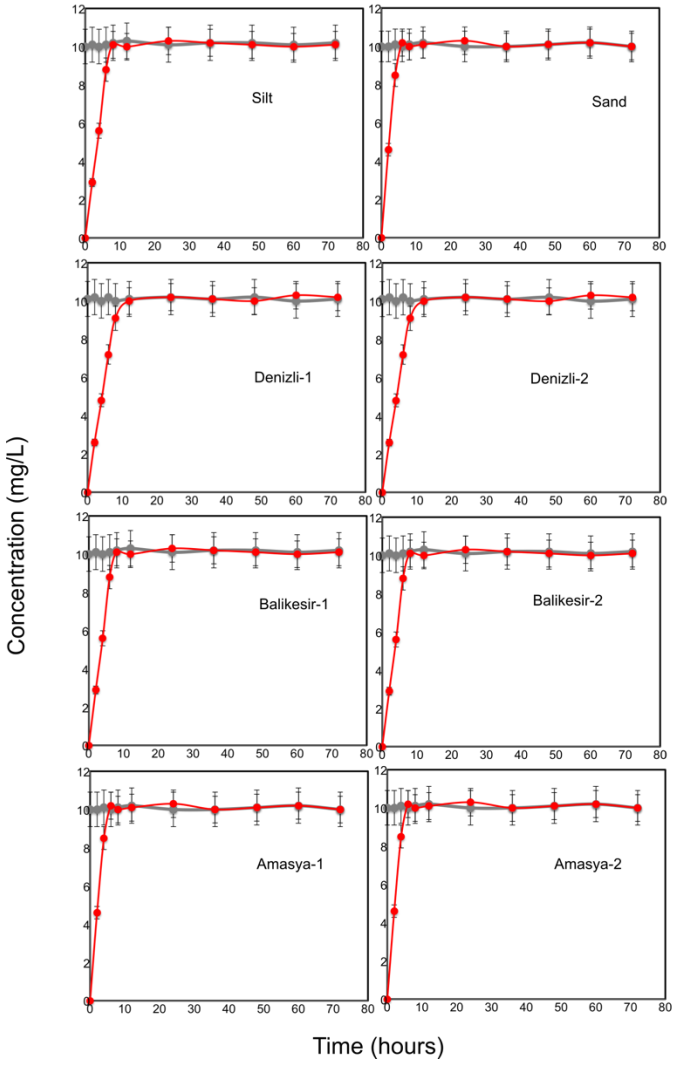

Figure 3 Influent (grey) and effluent (red) concentrations of atrazine (in mg/L) in abiotic columns filled with different types of soil. All the samples were prepared and measured in duplicates and error bars are the standard deviation between the measurements.

All the active columns showed biodegradation (Figure 4). The increase of the concentration of the influent was an expected result since there is a stationary phase until microbial community is established in the column and that results in uncomplete degradation. Seeing a stable output of the effluent indicated a steady state condition achieved in the column. The biodegradation capacities of the columns that were designed to represent topsoil was estimated by multiplying the flow rate of the feed with the difference between the influent and effluent concentrations in the column divided by the weight of the soil in the column. The biodegradation capacities for the 15 cm tall column ranged between 34 and 75 mg/kg/day for atrazine (Table 4). Similar biodegradation capacities were measured for every column because of the inoculation with the same mixture of microbial culture. To date, topsoil column studies were not performed for atrazine however, culture incubated studies were performed with various of isolates. The biodegradation rates in the studies where inoculated microcosms were analyzed, atrazine degradation ranged between 5-20 mg/kg/day [37-41, 44]. The column biodegradation rates of atrazine were higher than the reported microcosm biodegradation rates. The difference could be explained by a higher inoculation in the columns or sufficient oxygen presence during biodegradation because of a constant flow.

Biodegradability of atrazine in columns filled with soil samples were compared with the biodegradability in sand and silt filled columns to determine whether there was a relation between the sand and silt content of the soil, and biodegradation. No correlation was found between the biodegradation capacity of silt and sand columns and the silt and sand content in the soil columns. This finding indicated that the complexity of soil could not be simplified based on its sand or silt composition to estimate biodegradation capacity. The result was different than the previously published study stating that the biodegradability of a pesticide could be correlated with silt content of the soil [45]. The results of the current study showed that microbial activities should be measured for every sample of soil to be collected to estimate biodegradation capacity of atrazine.

Higher biodegradation rates obtained in the entire columns compared to the microcosms showed that topsoil readily degrades the pesticides within 15 cm of depth. When sufficient electron acceptor (oxygen), electron donor (pesticides) and microorganisms through inoculation is provided, the column was an ideal place for the organisms to biodegrade. Pesticides in the columns could not be completely degraded with the described optimal conditions, but their concentrations were decreased. Using pesticide-contaminated water for irrigation could decrease the concentration of

the pesticide and provide a sustainable remediation technique. Although it is a good practice to completely biodegrade the contaminants in the soil, it is not desirable by the users that all of the pesticides to be quickly biodegraded. This is because the effect of the pesticides would decrease when fast biodegradation occurs and other pesticide alternatives would be required to protect the crops in the field [46]. Therefore, a desirable outcome from this study was that a certain amount of chemicals remained in the columns and so it has been shown that the present methodology could be used not only to decrease the contamination but also to provide an alternative source of pesticides.

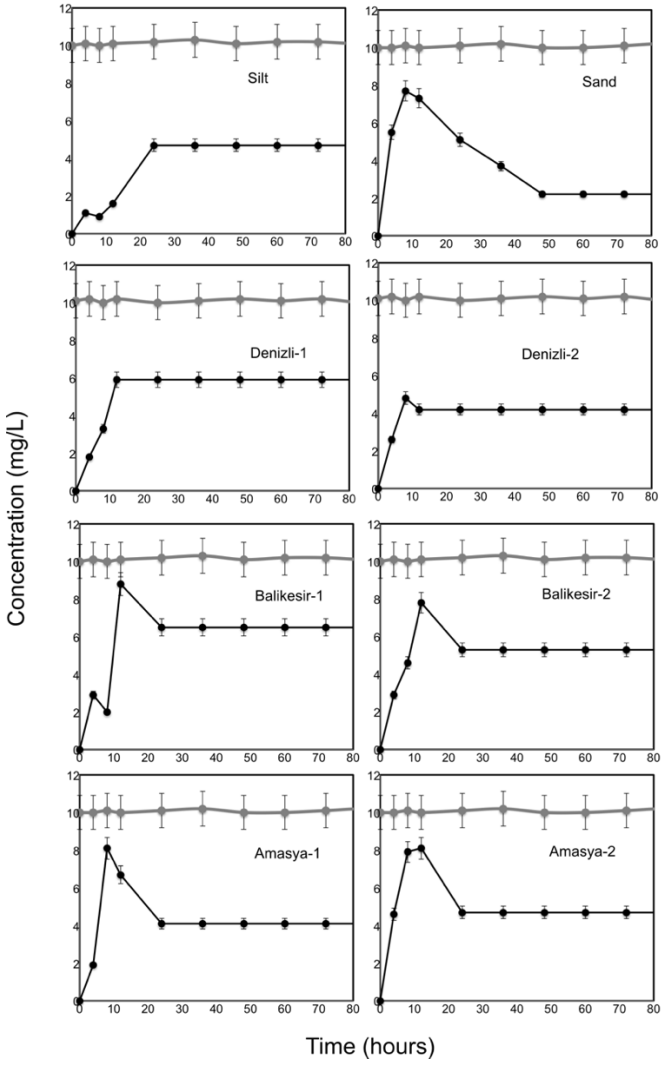

Figure 4 Influent (grey) and effluent (black) concentrations of atrazine (as in mg/L) in active columns filled with different types of soil. All the samples were prepared and measured in duplicates and error bars are the standard deviation between the measurements.

Table 4 Biodegradation capacities of the columns for atrazine (mg/kg/day)

	Silt	Sand	Denizli-1	Denizli-2
Atrazine	50 ± 6	75 ± 11	40 ± 5	56 ± 7
	Balikesir-1	Balikesir-2	Amasya-1	Amasya-2
Atrazine	34 ± 3	45 ± 6	56 ± 9	51 ± 8

3.4. Estimating the sustainable treatment capacity

A HYDRUS-1D simulation [23] was run for both atrazine using the adsorption/desorption amounts, porosities and biodegradation rates of the characterized field samples (Table 1-3). It was assumed that those parameters did not change throughout the 15 cm of the topsoil and that the governing mechanism was only the adsorption and desorption for the uptake of the pesticides between 15 cm and 3 m. The application of the pesticide was assumed to be via drip irrigation throughout the entire irrigation period with the concentrations of 33 mg/L of atrazine in water during the entire irrigation or until the maximum amount of the pesticide was reached. The choice of the irrigation was consistent with the applications for corn fields [47]. The model provided the output flux for the atrazine at the end of the 3 m, deep soil columns. Atrazine leaches to the groundwater was not detected for the drip irrigation system with a water flow of 60 ml/hr. or 2 l/hr. The results were similar in models both with or without biodegradation. These simulations have verified that pump and reuse is also a valid groundwater treatment methodology.

Known groundwater contamination concentrations were applied to the model to calculate how much atrazine would be reused with this method. Based on the model outputs, groundwater contaminated with 90 μg/L of atrazine would recover 4.5 kg/ha/year of atrazine. Amount is higher than the maximum limits of the pesticides in the field by allowable the United States Department of Agriculture [48, 49], indicating that if contaminated water is used for irrigation, additional pesticides will not be required for the field.

4. CONCLUSIONS

The present work showed that pump and reuse is a new technique that can remediate contaminated groundwater within the topsoil as long as proper microorganisms are present. Although this study did not include the effect of capillary fringe in the soil column, where the most biodegradation activity is seen [50-53], it was observed that the atrazine could be biodegraded. The results have shown that pump and reuse method is an employable treatment technique for contaminated groundwater and can provide a sustainable remediation. Furthermore, the study showed that a portion of the pesticides in the contaminated groundwater is adsorbed to the topsoil while the rest is biodegraded. Adsorbed pesticide could be reused for crop growth as shown by HYDRUS-1D simulation. Reusing pesticides with this method showed that pump and reuse technique can reduce pesticide use in the long run as long as drip irrigation is applied.

Drip irrigation flow rates is an important parameter for contaminant adsorption due to the contact time of the contaminant with the soil. In this study, drip irrigation rates did not change the infiltration within the 3 m column, but this is a parameter that could be crucial for different chemicals and needs to be addressed in future work. Similarly, it is important to consider that the groundwater is not always contaminated with a single contaminant and it is essential to understand the effect of combined contaminants prior to the water being reused, which requires further investigation for every soil and groundwater.

Overall, this study provided an unconventional sustainable remediation technique to apply contaminated water as irrigation water while the contaminants can be reused during crop growth and excess contamination can be degraded as long as active organisms are present in the soil. It is crucial to evaluate the soil for its potential prior to crop growth to reduce the risk on the crop yield and quality. Therefore, further studies need to be conducted to determine the crop yield and quality once contaminated groundwater is used to assure the outcome.

Acknowledgments

The authors would like to acknowledge the

support of Selim Canbazoglu and Carlos Alberto Donado Morcillo.

Funding

This study was supported by ODTU BAP Project number YOP-311-2018-2828, TUBITAK Project number 118C013, Turkey and by El Sistema Nacional de Investigación (*SNI*) (National Scientist Membership) SNI No. 10-2018, SENACYT, Panama City, Panama.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

The author wrote and conducted the study.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

REFERENCES

[1] A. Abdullah, S. Brobst, I. Pervaiz, M. Umer, and A. Nisar, "Learning dynamics of pesticide abuse through data mining," in Proceedings of the second workshop on Australasian information security, Data Mining and Web Intelligence, and Software Internationalisation-Volume 32, 2004: Australian Computer Society, Inc., pp. 151-156.

[2] D. I. Gustafson, "Groundwater ubiquity score: a simple method for assessing pesticide leachability," Environmental Toxicology and Chemistry: An International Journal, vol. 8, no. 4, pp. 339-357, 1989.

[3] Y. Zhao and Y. Pei, "Risk evaluation of groundwater pollution by pesticides in China: a short review," Procedia Environmental Sciences, vol. 13, pp. 1739-1747, 2012.

[4] D. L. Hoag and A. G. Hornsby, "Coupling groundwater contamination with economic returns when applying farm pesticides," Journal of environmental quality, vol. 21, no. 4, pp. 579-586, 1992.

[5] C. Niti, S. Sunita, K. Kamlesh, and K. Rakesh, "Bioremediation: An emerging technology for remediation of pesticides," Research Journal of Chemistry and Environment, vol. 17, p. 4, 2013.

[6] C. Kao, C. Chai, J. Liu, T. Yeh, K. Chen, and S. Chen, "Evaluation of natural and enhanced PCP biodegradation at a former pesticide manufacturing plant," Water research, vol. 38, no. 3, pp. 663-672, 2004.

[7] D. K. Singh, "Biodegradation and bioremediation of pesticide in soil: concept, method and recent developments," Indian journal of microbiology, vol. 48, no. 1, pp. 35-40, 2008.

[8] W. A. Jury, D. D. Focht, and W. J. Farmer, "Evaluation of Pesticide Groundwater Pollution Potential from Standard Indices of Soil-Chemical Adsorption and Biodegradation 1," Journal of environmental quality, vol. 16, no. 4, pp. 422-428, 1987.

[9] X. Zhang, X. Zhu, R. Chen, S. Deng, R. Yu, and T. Long, "Assessment of Biodegradation in Natural Attenuation Process of Chlorinated Hydrocarbons Contaminated Site: An Anaerobic Microcosm Study," Soil and Sediment Contamination: An International Journal, vol. 29, no. 2, pp. 165-179, 2020.

[10] G. Hatipoglu and Z. Kurt, "Modeling irrigation with nitrate contaminated groundwater," Pamukkale Univ Muh Bilim Derg, vol. 1000, no. 1000, pp. 0-0, 2019, doi: 10.5505/pajes.2019.38963.

[11] U. Dorigo, X. Bourrain, A. Berard, and C. Leboulanger, "Seasonal changes in the sensitivity of river microalgae to atrazine and isoproturon along a contamination gradient," Science of the Total Environment, vol. 318, no. 1-3, pp. 101-114, 2004.

[12] D. Belluck, S. Benjamin, and T. Dawson, "Groundwater contamination by atrazine and its metabolites: risk assessment, policy, and legal implications," ACS Publications, 1991.

[13] A. Gawel, B. Seiwert, S. Sühnholz, M. Schmitt-Jansen, and K. Mackenzie, "In-situ treatment of herbicide-contaminated groundwater-Feasibility study for the cases atrazine and bromacil using two novel nanoremediation-type materials," Journal of Hazardous Materials, p. 122470, 2020.

[14] K. Jayachandran, T. Steinheimer, L. Somasundaram, T. B. Moorman, R. S. Kanwar, and J. R. Coats, "Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow

groundwater," Journal of environmental quality, vol. 23, no. 2, pp. 311-319, 1994.

[15] H. Pionke and D. Glotfelty, "Contamination of groundwater by atrazine and selected metabolites," Chemosphere, vol. 21, no. 6, pp. 813-822, 1990.

[16] R. Wauchope, "The pesticide content of surface water draining from agricultural fields—a review 1," Journal of environmental quality, vol. 7, no. 4, pp. 459-472, 1978.

[17] S. Beegum, J. Vanderborght, J. Šimůnek, M. Herbst, K. Sudheer, and I. M. Nambi, "Investigating Atrazine Concentrations in the Zwischenscholle Aquifer Using MODFLOW with the HYDRUS-1D Package and MT3DMS," Water, vol. 12, no. 4, p. 1019, 2020.

[18] Cornell University College of Agricultural and Life Sciences. "Atrazine Application Rates." Cornell University College of Agricultural and Life Sciences. https://fieldcrops.cals.cornell.edu/corn/weed-control-corn/atrazine-application-rates/ (accessed 13/11/19, 2019).

[19] J. Bethsass and A. Colangelo, "European Union bans atrazine, while the United States negotiates continued use," International journal of occupational and environmental health, vol. 12, no. 3, pp. 260-267, 2006.

[20] P. K. Kalita, R. S. Kanwar, J. L. Baker, and S. W. Melvin, "Groundwater residues of atrazine and alachlor under water-table management practices," Transactions of the ASAE, vol. 40, no. 3, pp. 605-614, 1997.

[21] S. K. Abd-Elmabod et al., "Modeling agricultural suitability along soil transects under current conditions and improved scenario of soil factors," in Soil mapping and process modeling for sustainable land use management: Elsevier, 2017, pp. 193-219.

[22] Solar dripper. "Drip irrigation efficiency and water saving." https://solar-dripper.com/en/drip-irrigation-efficiency/ (accessed 15/11/19, 2019).

[23] J. Šimůnek, M. T. Van Genuchten, and M. Šejna, "Recent developments and applications of the HYDRUS computer software packages," Vadose Zone Journal, vol. 15, no. 7, 2016.

[24] M. G. Bos, "Water requirements for irrigation and the environment," 2018.

[25] S. S. Staff, "Soil survey manual," 1993.

[26] R. D. Horrocks and J. F. Valentine, Harvested forages. Academic Press, 1999.

[27] L. Yue, C. Ge, D. Feng, H. Yu, H. Deng, and B. Fu, "Adsorption–desorption behavior of atrazine on agricultural soils in China," Journal of Environmental Sciences, vol. 57, pp. 180-189, 2017.

[28] S. A. Clay and W. C. Koskinen, "Characterization of alachlor and atrazine desorption from soils," Weed Science, pp. 74-80, 1990.

[29] J. C. Spain, J. B. Hughes, and H.-J. Knackmuss, Biodegradation of nitroaromatic compounds and explosives. CRC Press, 2000.

[30] S. Nasseri, M. Dehghani, S. Amin, K. Naddafi, and Z. Zamanian, "Fate of atrazine in the agricultural soil of corn fields in Fars province of Iran," Journal of Environmental Health Science & Engineering, vol. 6, no. 4, pp. 223-232, 2009.

[31] A. Hildebrandt, S. Lacorte, and D. Barceló, "Assessment of priority pesticides, degradation products, and pesticide adjuvants in groundwaters and top soils from agricultural areas of the Ebro river basin," Analytical and

bioanalytical chemistry, vol. 387, no. 4, pp. 1459-1468, 2007.

[32] S. Rousseaux, A. Hartmann, and G. Soulas, "Isolation and characterisation of new Gram-negative and Gram-positive atrazine degrading bacteria from different French soils," FEMS Microbiology Ecology, vol. 36, no. 2-3, pp. 211-222, 2001.

[33] N. Udiković-Kolić, C. Scott, and F. Martin-Laurent, "Evolution of atrazine-degrading capabilities in the environment," Applied microbiology and biotechnology, vol. 96, no. 5, pp. 1175-1189, 2012.

[34] L. E. Erickson, K. H. Lee, and D. D. Sumner, "Degradation of atrazine and related s-triazines," Critical Reviews in Environmental Science and Technology, vol. 19, no. 1, pp. 1-14, 1989.

[35] M. Radosevich, S. J. Traina, Y.-L. Hao, and O. H. Tuovinen, "Degradation and mineralization of atrazine by a soil bacterial isolate," Applied and Environmental Microbiology, vol. 61, no. 1, pp. 297-302, 1995.

[36] X. Fan and F. Song, "Bioremediation of atrazine: recent advances and promises," Journal of soils and sediments, vol. 14, no. 10, pp. 1727-1737, 2014.

[37] S. Sagarkar et al., "Monitoring bioremediation of atrazine in soil microcosms using molecular tools," Environmental pollution, vol. 172, pp. 108-115, 2013.

[38] L. Pussemier, S. Goux, V. Vanderheyden, P. Debongnie, I. Tresinie, and G. Foucart, "Rapid dissipation of atrazine in soils taken from various maize fields," Weed Research, vol. 37, no. 3, pp. 171-179, 1997.

[39] M. Dehghani, S. Nasseri, and H. Hashemi, "Study of the bioremediation of atrazine under variable carbon and nitrogen sources by mixed bacterial consortium isolated from corn field soil in Fars Province of Iran," Journal of environmental and public health, vol. 2013, 2013.

[40] H. Fang, J. Lian, H. Wang, L. Cai, and Y. Yu, "Exploring bacterial community structure and function associated with atrazine biodegradation in repeatedly treated soils," Journal of hazardous materials, vol. 286, pp. 457-465, 2015.

[41] I. Mirgain, G. Green, and H. Monteil, "Degradation of atrazine in laboratory microcosms: isolation and identification of the biodegrading bacteria," Environmental Toxicology and Chemistry: An International Journal, vol. 12, no. 9, pp. 1627-1634, 1993.

[42] M. Kah, S. Beulke, and C. D. Brown, "Factors influencing degradation of pesticides in soil," Journal of agricultural and food chemistry, vol. 55, no. 11, pp. 4487-4492, 2007.

[43] H. Patel, "Fixed-bed column adsorption study: a comprehensive review," Applied Water Science, vol. 9, no. 3, pp. 1-17, 2019.

[44] D. Lima et al., "Evaluating a bioremediation tool for atrazine contaminated soils in open soil microcosms: the effectiveness of bioaugmentation and biostimulation approaches," Chemosphere, vol. 74, no. 2, pp. 187-192, 2009.

[45] M. S. Rodríguez-Cruz, J. E. Jones, and G. D. Bending, "Field-scale study of the variability in pesticide biodegradation with soil depth and its relationship with soil characteristics," Soil Biology and Biochemistry, vol. 38, no. 9, pp. 2910-2918, 2006.

[46] C. A. Damalas and I. G. Eleftherohorinos, "Pesticide exposure, safety issues, and

risk assessment indicators," International journal of environmental research and public health, vol. 8, no. 5, pp. 1402-1419, 2011.

[47] F. R. Lamm and T. P. Trooien, "Subsurface drip irrigation for corn production: a review of 10 years of research in Kansas," Irrigation science, vol. 22, no. 3-4, pp. 195-200, 2003.

[48] F. Ackerman, "The economics of atrazine," International Journal of Occupational and Environmental Health, vol. 13, no. 4, pp. 437-445, 2007.

[49] J. Fernandez-Cornejo, R. F. Nehring, C. Osteen, S. Wechsler, A. Martin, and A. Vialou, "Pesticide use in US agriculture: 21 selected crops, 1960-2008," USDA-ERS Economic Information Bulletin, no. 124, 2014.

[50] Z. Kurt, E. E. Mack, and J. C. Spain, "Biodegradation of cis-dichloroethene and vinyl chloride in the capillary fringe," Environmental science & technology, vol. 48, no. 22, pp. 13350-13357, 2014.

[51] Z. Kurt, E. E. Mack, and J. C. Spain, "Natural attenuation of nonvolatile contaminants in the capillary fringe," Environmental science & technology, vol. 50, no. 18, pp. 10172-10178, 2016.

[52] Z. Kurt and J. C. Spain, "Biodegradation of chlorobenzene, 1, 2-dichlorobenzene, and 1, 4-dichlorobenzene in the vadose zone," Environmental science & technology, vol. 47, no. 13, pp. 6846-6854, 2013.

[53] J. Luo, Z. Kurt, D. Hou, and J. C. Spain, "Modeling aerobic biodegradation in the capillary fringe," Environmental science & technology, vol. 49, no. 3, pp. 1501-1510, 2015.