Environmental Pollution: Health Effects and Operational Implications for Pollutants Removal

Guest Editors: Roya Kelishadi, Mohammad Mehdi Amin, Tuula Anneli Tuhkanen, Rainer Schulin, and Ajay Kumar Gupta
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Contents

Environmental Pollution: Health Effects and Operational Implications for Pollutants Removal, Roya Kelishadi
Volume 2012, Article ID 341637, 2 pages

Study of Heavy Metal Levels among Farmers of Muda Agricultural Development Authority, Malaysia, Ahmad Rohi Ghazali, Nur Ezzuzullanie Abdul Razak, Mohd Sham Othman, Hidayatulfath Othman, Ismarulyusda Ishak, Syarif Husin Lubis, Nihayah Mohammad, Zariyantey Abd Hamid, Zaliha Harun, Firdaus Kamarulzaman, and Rozaini Abdullah
Volume 2012, Article ID 758349, 4 pages

Comparison of Size and Geography of Airborne Tungsten Particles in Fallon, Nevada, and Sweet Home, Oregon, with Implications for Public Health, Paul R. Sheppard, Brian J. Bierman, Kent Rhodes, Gary Ridenour, and Mark L. Witten
Volume 2012, Article ID 509458, 8 pages

Wider Action Plan and Multidisciplinar Approach Could Be a Wining Idea in Creation of Friendly Environment, Natasa Gojkovic-Bukvic and Nenad Bukvic
Volume 2012, Article ID 473427, 7 pages

Effects of Three Types of Oil Dispersants on Biodegradation of Dispersed Crude Oil in Water Surrounding Two Persian Gulf Provinces, Azadeh Zolfaghari-Baghbaderani, Mozhgan Emtyazjoo, Parinaz Pourafia, Sedigheh Mehrabian, Samira Bijani, Daryoush Farkhani, and Parisa Mirmoghhtadaee
Volume 2012, Article ID 981365, 8 pages

Environmental Impact Assessment of the Industrial Estate Development Plan with the Geographical Information System and Matrix Methods, Mohammad Ghasemian, Parinaz Poursafa, Mohammad Mehdi Amin, Mohammad Ziarati, Hamid Ghoddousi, Seyyed Alireza Momeni, and Amir Hossein Rezaei
Volume 2012, Article ID 407162, 8 pages

Ethylbenzene Removal by Carbon Nanotubes from Aqueous Solution, Bijan Bina, Hamidreza Pourzamani, Alimorad Rashidi, and Mohammad Mehdi Amin
Volume 2012, Article ID 817187, 8 pages

Community-Led Assessment of Risk from Exposure to Mercury by Native Amerindian Wayana in Southeast Suriname, Daniel Peplow and Sarah Augustine
Volume 2012, Article ID 674596, 10 pages

Evaluation of Trace Metal Levels in Tissues of Two Commercial Fish Species in Kapar and Mersing Coastal Waters, Peninsular Malaysia, Fathi Alhashmi Bashir, Mohammad Shuhaimi-Othman, and A. G. Mazlan
Volume 2012, Article ID 352309, 10 pages

Involuntary and Persistent Environmental Noise Influences Health and Hearing in Beirut, Lebanon, Marjaneh M. Fooladi
Volume 2012, Article ID 235618, 7 pages
Environmental pollution is reaching worrying proportions worldwide. Urbanization and industrialization along with economic development have led to increased energy consumption and waste discharges. The global environmental pollution, including greenhouse gas emissions and acid deposition, as well as water pollution and waste management, is considered as international public health problems, which should be investigated from multiple perspectives including social, economic, legislation, and environmental engineering systems, as well as lifestyle habits helping health promotion and strengthening environmental systems to resist contamination [1–3].

Environmental pollutants have various adverse health effects from early life; some of the most important harmful effects are perinatal disorders, infant mortality, respiratory disorders, allergy, malignancies, cardiovascular disorders, increase in stress oxidative, endothelial dysfunction, mental disorders, and various other harmful effects [4, 5]. Though, short-term effects of environmental pollutants are usually highlighted, wide range of hazards of air pollution from early life and their possible implication on chronic non-communicable diseases of adulthood should be underscored. Numerous studies have exposed that environmental particulate exposure has been linked to increased risk of morbidity and mortality from many diseases, organ disturbances, cancers, and other chronic diseases [6, 7]. Therefore, it is time to take action and control the pollution. Otherwise, the waste products from consumption, heating, agriculture, mining, manufacturing, transportation, and other human activities will degrade the environment.

Based on the strength of the scientific knowledge regarding the adverse health effects of environmental pollution and the magnitude of their public health impact, different kinds of interventions should be taken into account. In addition to industrial aspects, the public awareness should be increased in this regard. Likewise, health professionals have an exclusive competency to help for prevention and reduction of the harmful effects of environmental factors, this capacity should be underscored in their usual practice.

This special issue is dedicated to increasing the depth of research across all areas of health effects of pollutants in air, water, and soil environments, as well as new techniques for their measurement and removal. The goal of the special issue is to familiarize the readership of the Journal of Environmental and Public Health with the potential for different aspects of environmental pollution. We expect this special issue would appeal to researchers, public health practitioners, and policymakers.

Roya Kelishadi

References


Research Article

Study of Heavy Metal Levels among Farmers of Muda Agricultural Development Authority, Malaysia

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Heavy metals, particularly cadmium, lead, and arsenic, constitute a significant potential threat to human health. This study was conducted to determine the levels of cadmium, lead, and arsenic in nail samples from farmers at Muda Agricultural Development Authority (MADA), Kedah, Malaysia, and evaluate factors that can contribute to their accumulations. A total of 116 farmers participated in this study. Inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze concentration of heavy metals in the nail samples and questionnaires were given to participants to get demographic, health status, and their agricultural activities data. In this paper, the level of heavy metals was within the normal range and varies according to demographic factors.

We found that there were significant correlations between working period with level of lead and arsenic ($r = 0.315$ and $r = 0.242$, resp., $P < 0.01$) and age with lead level ($r = 0.175$, $P < 0.05$). Our findings suggested that agricultural activities could contribute to the accumulation of heavy metals in farmers. Hence, the control of environmental levels of and human exposure to these metals to prevent adverse health effects is still an important public health issue.

1. Introduction

Farmers are exposed to a variety of pollutants particularly heavy metals that are released into the environment as a consequence of agricultural activities such as the use of pesticides and fertilizers. Some metals are extremely toxic to humans and the toxic heavy metals of greatest concern include cadmium, lead, and arsenic [1]. These heavy metals are incorporated into the organism via different routes and can then be stored and distributed in different tissues which lead to an internal bioconcentration that can induce different alterations, adverse effects, and/or diseases [2, 3].

Therefore, it is important to determine the heavy metals concentration in occupationally exposed workers to monitor and assess their impact on human health. The use of human nail as a biomarker in occupational exposure to pollutants is an alternative biomarker besides blood and urine [4]. Nail is a good biomarker for several toxic elements in which the subjects had been exposed to these elements for the duration of 2 to 18 months [5]. Apart from that it is also a useful tool to measure the level of pollutants for long-term exposure [6]. According to International Atomic Energy Agency [7], human exposure to heavy metal at low level is a condition where it could cause poisoning and diseases, whereas accidental exposure at high level could cause serious effect immediately [8].

In this study, the levels of cadmium, lead, and arsenic in nail samples from farmers were determined and those levels were then correlated with their demographic factors,
blood pressure, and also their smoking working period and smoking habit.

2. Materials and Methods

2.1. Study Group. Subjects for this study were farmers working at the Wilayah III (Pendang, Kedah,) and Wilayah IV (Kota Sarang Semut, Kedah,) of MADA, Malaysia, who were chosen via universal sampling from a list of registered farmer under MADA authority. A total of 116 male Malay farmers took part in this study. Inclusion criteria of subjects for this study consisted of farmers that had been working more than one year and less than 60 years of age. The study protocol was approved and conducted in accordance with the Ethical Principles for Medical Research Involving Human Subjects as defined by the research institution.

2.2. Questionnaire. Questionnaires were used to collect demographic data and factors that can influence the levels of heavy metals in the samples. Each subject was asked on the sections listed in the questionnaire which included (A) personal background, (B) awareness of illness, and (C) agricultural activities.

2.3. Sample Analysis. All glassware and plastic equipments were immersed in nitric acid solution overnight to avoid contamination. Then, all the equipments were rinsed with deionized water, dried, and stored appropriately. Soil and dirt were removed from the nail sample using the method recommended by the International Atomic Energy Agency [9] with slight modifications [10, 11]. The samples were then rinsed thoroughly with deionized water and placed in the desiccator for drying processes and stored in sealed plastic bags at room temperature until further processing was carried out.

Then, a total of 10–20 mg samples were weighed using electronic scales and placed in a porcelain bowl that had been cleaned. Samples were then heated on a heating plate (Stuart Scientific, UK) until the ash was formed [11]. After cooling, the ash samples were moistened with 0.5 mL deionized water, and then 1 mL of nitric acid and 0.5 mL perchloric acid were added accordingly. Then, the samples were heated up to dry on a heating plate (Stuart Scientific, UK) at a temperature of 20°C. About 0.5 mL of nitric acid and deionized water are added into the resulting residues and heated for 5 minutes until a clear solution was formed. This solution was rinsed in 10 mL volumetric flask with deionized water until the final volume of 10 mL. Samples were stored in metal-free plastic tubes at room temperature until the determination of the level of heavy metals was conducted using ICP-MS (PerkinElmer, USA) [12].

2.4. Statistical Analysis. Descriptive analysis was conducted to obtain means, standard deviations, and range of heavy metals in the nail samples. We employed one-way ANOVA test to compare the means between heavy metals according to blood pressure and smoking habit. On the other hands, to find the correlation of the heavy metals with age and working period, we employed the Spearman correlation test because the data for these variables were not normally distributed. All the data collected were analyzed statistically using SPSS software version 17.0.

3. Results and Discussion

The influence of environmental pollution on human health can be determined in terms of biomonitoring of the metabolically inactive tissues such as nails due to easy of sample collection, transportation, storage, and preparation for analysis. Blood and urine could be alternative biomarkers but these samples are meant for short-term exposure [4].

In our findings, the average levels of cadmium, lead, and arsenic (µg/g) in the nail samples from the MADA farmers are presented in Table 1. Since there was an insufficient reference on baseline data of the levels of heavy metals in Malaysian population study, we compared our results with other similar studies from other countries. Table 2 shows comparison of means ± standard deviations of cadmium, lead, and arsenic (µg/g) levels in nail samples from references with similar studies from other countries.

Table 1: Levels of cadmium, lead, and arsenic (µg/g) in the nail sample of MADA farmers.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Mean concentration (mean ± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>0.874 ± 0.746</td>
</tr>
<tr>
<td>Lead</td>
<td>6.611 ± 5.170</td>
</tr>
<tr>
<td>Arsenic</td>
<td>7.801 ± 3.184</td>
</tr>
</tbody>
</table>

Table 2: Comparison of means ± standard deviations of cadmium, lead, and arsenic (µg/g) levels in nail samples from references with similar studies from other countries.

<table>
<thead>
<tr>
<th>References</th>
<th>Mean concentration (mean ± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>Cadmium (Cd)</td>
</tr>
<tr>
<td>[13]</td>
<td>2.50 ± 1.70</td>
</tr>
<tr>
<td>[14]</td>
<td>1.35 ± 0.85</td>
</tr>
<tr>
<td>[5]</td>
<td>0.32 ± 0.09</td>
</tr>
</tbody>
</table>

ND: not detected.

Table 3 shows the average levels of cadmium, lead, and arsenic in farmers according to their blood pressure and smoking working period. Results from this study showed that there...
was no significant difference in the levels of heavy metals in normal and high blood pressure groups. A study conducted by Sukumar and Subramanian [16] also found that there was no significant difference for cadmium and lead levels among subjects with high blood pressure and normal blood pressure. For arsenic, there was also no significant difference between subjects with high blood pressure and normal blood pressure groups. Other factors such as dietary intake might influence the levels of heavy metals in the nail samples of the subjects in our study.

Smoking is also associated with high blood pressure and heavy metal content [17]. This could be due to the cadmium and other heavy metals content in the cigarettes [18]. Results from Sukumar and Subramanian [16] and Mortada et al. [14] studies found that cadmium levels were significantly higher among subjects who smoked. However, this study showed that levels of cadmium did not differ significantly (P > 0.05) among smokers and nonsmokers groups. Levels of lead and arsenic also showed no significant difference (P > 0.05) between smokers and nonsmokers. Studies conducted by Sukumar and Subramanian [16] also found that lead levels were not influenced by smoking.

Table 4 shows the relationships between the farmers’ age and level of heavy metals from their nail samples. There was no significant relationship between both cadmium and arsenic levels with age (r = −0.045 and r = 0.124, resp., P > 0.05) according to the Spearman correlation test. However, the analysis of the relationship between the age and levels of lead showed a significant relationship (r = 0.175, P < 0.05). A study conducted by Rodushkin and Axelsson [19] showed that age did not influence the levels of heavy metals in the nail samples. Lead levels were also found to be increased among older individuals than younger individuals [14].

Table 4 also shows the relationships between working period as farmers and level of heavy metals in their nail samples. This study found that there was no relationship between cadmium level and their working period as farmers (r = 0.0117, P > 0.05). Cadmium accumulates primarily in liver and kidney in which it would bind to metallothionein [20]. This might be the reason for the insignificant difference between the cadmium level in the nail samples and their working period. However, there was a significant relationship between working period as a farmer and the level of lead and arsenic among MADA farmers (r = 0.315 and r = 0.242, resp., P < 0.01). Faridah et al. [21] stated that cadmium and lead were potential bioaccumulators because of their long half-lives. Most farmers who had been working for 20–30 years and exposed to pesticides and fertilizers could increase the levels of heavy metals in their bodies [15].

In addition, data collected from questionnaires showed that almost 95% of subjects used protective equipment when working. Protective equipment is a tool to reduce exposure and prevent harm including heavy metals material from entering the body. Ironically, in this study we found that the level of arsenic was still high among the subjects. While assessing the heavy metals exposure, other factors such as nutrition, socioeconomic status, exposure conditions, genetic variability and susceptibility, have to be considered for a realistic approach.

### 4. Conclusion

There were significant correlations between heavy metals with subject’s age and working period as farmers. However, there was no significant correlation between heavy metals and their blood pressure and smoking habits. Hence, exposure of heavy metals to the farmers could be due to the use of pesticides and fertilizers in various agricultural activities. The control of environmental levels of and human exposure to these metals to prevent adverse health effects is still an important public health issue and other alternatives to control use of fertilizers and reducing the pesticides applications have to be implemented.
Acknowledgment

Special thanks to Muda Agricultural Development Authority (MADA), Kedah, Malaysia, for the permission to conduct this study on farmers under their authority.

References


Comparison of Size and Geography of Airborne Tungsten Particles in Fallon, Nevada, and Sweet Home, Oregon, with Implications for Public Health

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To improve understanding of possible connections between airborne tungsten and public health, size and geography of airborne tungsten particles collected in Fallon, Nevada, and Sweet Home, Oregon, were compared. Both towns have industrial tungsten facilities, but only Fallon has experienced a cluster of childhood leukemia. Fallon and Sweet Home are similar to one another by their particles of airborne tungsten being generally small in size. Meteorologically, much, if not most, of residential Fallon is downwind of its hard metal facility for at least some fraction of time at the annual scale, whereas little of residential Sweet Home is downwind of its tungsten facility. Geographically, most Fallon residents potentially spend time daily within an environment containing elevated levels of airborne tungsten. In contrast, few Sweet Home residents potentially spend time daily within an airborne environment with elevated levels of airborne tungsten. Although it cannot be concluded from environmental data alone that elevated airborne tungsten causes childhood leukemia, the lack of excessive cancer in Sweet Home cannot logically be used to dismiss the possibility of airborne tungsten as a factor in the cluster of childhood leukemia in Fallon. Detailed modeling of all variables affecting airborne loadings of heavy metals would be needed to legitimately compare human exposures to airborne tungsten in Fallon and Sweet Home.

1. Introduction

Size and geography of airborne tungsten particles collected in Fallon, Nevada, and Sweet Home, Oregon (Figure 1), were compared as part of ongoing research on the cooccurrence of airborne tungsten and a cluster of childhood leukemia in Fallon. Fallon experienced a cluster of childhood leukemia beginning in 1997 [3], with the last case announced in 2004 [4]. Although the cluster is thought to have abated [5], at least one additional case of childhood leukemia has occurred in Fallon since 2004 [6]. Given Fallon’s pediatric population of about 2500 children up to 19 years in age [1], and a national expected rate of childhood leukemia of 4.1 cases per 100,000 children up to 19 years in age per year [7], the expected rate of childhood leukemia for Fallon should be only one case every ten years.

This cluster, deemed “one of the most unique … ever reported” [8], prompted extensive research in an effort to find a cause. Among other findings, multiple lines of evidence have shown that Fallon has elevated levels of airborne tungsten and cobalt [9–13].

Although Nevada is naturally rich in tungsten minerals, including geologically [14] and hydrologically [15, 16], Fallon also has a potential anthropogenic source of airborne tungsten. An industrial facility specializing in hard-metal metallurgy, which uses tungsten carbide and cobalt to produce tool materials [17], is located within Fallon. This hard-metal facility was named by the Nevada State Health Division as a candidate source of tungsten in Fallon [18]. Morphological and chemical characteristics of airborne tungsten particles in Fallon indicate that they are anthropogenic in origin, not natural [19].
TABLE 1: Geographical comparison between Fallon and Sweet Home.

<table>
<thead>
<tr>
<th>Community</th>
<th>Population</th>
<th>No. of employees in tungsten facility</th>
<th>Annual temperature (°C)</th>
<th>Annual precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fallon</td>
<td>7,536</td>
<td>~100b</td>
<td>11.2</td>
<td>135</td>
</tr>
<tr>
<td>Sweet Home</td>
<td>8,016</td>
<td>11c</td>
<td>11.6</td>
<td>1,397</td>
</tr>
</tbody>
</table>

a From [1].
b From [2].
c Personal communication with facility manager.

2. Materials and Methods

2.1. Fallon and Sweet Home. Fallon and Sweet Home are similar in that both are rural towns with small populations of about 8,000 people (Table 1), and both towns have industrial facilities that process or otherwise use fine tungsten particles. Based on number of employees, the Fallon tungsten facility is larger than that of Sweet Home. Fallon and Sweet Home have similar annual mean temperatures (~11 °C), but Sweet Home receives 10 times more rainfall than Fallon on average.

2.2. Air Sampling. In March and November, 2004, airborne dust was collected within Fallon using portable, high-volume particulate air samplers [9]. Weather during these collection periods was generally sunny and windy in March and rainy in November. The filter type was glass-fiber, a common medium for high-volume sampling of airborne particulates [21, 22]. Filters were 510 µm thick and had up to 99.99% retention for particles down to sub-µm sizes [23]. In May, 2005, airborne dust was collected within Sweet Home using the same equipment used in Fallon [20]. Weather during this collection period was generally sunny and calm.

For the particle size part of this research, three filters were selected from both Fallon and Sweet Home for further measurement and analysis. The filters were selected to optimize a transect of distance from their respective industrial tungsten facilities.

2.3. Additional Sampling in Sweet Home. Two additional samples of tungsten-laden dust were collected in 2011 in Sweet Home. One, dust was collected from the powder drum itself, which was not the actual product of the industrial facility but rather the fine waste that results from its processing. This allowed assessment of tungsten particles that
result from the production process. Two, surface dust was swept up from pavement just east of the facility. This allowed assessment of airborne tungsten particles that drift out of the building but do not travel far from the source.

2.4. Isolation of Tungsten Particles. To remove the collected particulate matter from the glass-fiber filters for microanalysis, a 20 cm² portion of each filter was placed into its own 50 mL plastic centrifuge tube with approximately 10 mL of ethanol. The tubes were sonicated for 20 minutes to dislodge the particles, and then the filter pieces were removed from the tubes and saved. Approximately 50 mg of the powder drum and surface dust samples was placed into their own centrifuge tubes, again with approximately 10 mL of ethanol.

Fifteen mL of methyl iodide was added to the centrifuge tubes, and the samples were centrifuged for 10 minutes at 2000 rpm. The ethanol layer was pipetted off and saved. The bottom methyl iodide layer was filtered on 25-millimeter polyester membrane filters and mounted onto aluminum stubs.
for automated analysis. This method recovers a representative sample for particle sizing and chemical analysis and has worked specifically with tungsten particles in prior work [19].

2.5. Automated Particle Analysis. Samples were analyzed using an ASPEX 3025 personal scanning electron microscope (PSEM) utilizing energy dispersive X-ray spectrometry (EDS) and ASPEX’s automated feature analysis (AFA) software. This system and software located, counted, measured, and quantitatively analyzed particles in fully automated mode. Particles containing less than 80% tungsten were culled out of the data set. Frequency histograms plotting the size of tungsten particles were generated, and images of representative particles were collected. Calibration was performed using (1) a certified tungsten standard from Geller Microanalysis Laboratory for tungsten quantification, (2) a copper standard for energy scaling, and (3) a commercial standard (PGS) from Aspex LLC for particle sizing.

2.6. Geographical Analysis. Aerial photos of both towns were labeled with limits of residential areas, locations of respective industrial tungsten facilities, and circles of elevated levels of airborne tungsten. Prevailing wind directions of both towns were illustrated with wind rose diagrams using data from nearby weather stations.

3. Results and Discussion

3.1. Tungsten Particles from Air Filters. The size distributions of tungsten particles are similar across all six air filters from both towns. Median sizes of tungsten particles across all air filters range from 1.22 to 1.83 µm in diameter (Figures 2(a)–2(f)). This size class (<2.1 µm) is typical for airborne particulates of heavy metals [24]. The particulate size class of 1 to 2 µm in diameter is also considered seriously threatening to human health [25]. Additionally, the vast majority of tungsten particles isolated from both towns air filters were below 5 µm in size (Figures 2(a)–2(f)). The Sweet Home filters also contained tungsten particles considerably larger than the median size, ranging up to 21 µm in diameter, but very particles were this large.

3.2. Tungsten Particles from the Powder Drum and Surface Dust in Sweet Home. The vast majority of tungsten particles collected from the powder drum and surface dust samples of Sweet Home were below 5 µm in size (Figures 2(g)–2(h)). Median particle sizes were ~1.50 µm in both cases. In general, the size distributions of tungsten particles of these nonairborne samples are similar to the airborne samples of Sweet Home, illustrating that airborne tungsten particles collected with air filters accurately reflect the size distribution of tungsten particles at the industrial source.
Figure 4: Aerial view of Sweet Home, Oregon, with the 400-m distance centered on the tungsten facility. The red boundary marks the limit of residential Sweet Home.

Maximum particle size from the drum sample was just over 50 µm (Figure 2(g)), accurately reflecting the large target particle size of the manufacturer (personal communication with the facility manager). Maximum particle size from the surface dust sample was smaller (Figure 2(h)), just under 30 µm, accurately reflecting that large, dense airborne particles do not travel as far as smaller particles [26].

3.3. Geographical Location of Tungsten Facilities Relative to Their Towns. Fallon is relatively circular in layout, more or less centered on the crossroads of two highways (Figure 3). The hard metal facility of Fallon is located just northwest of the crossroads. Airborne tungsten loadings within 3 km of the hard metal facility can be elevated above loadings farther away that can be considered as background levels [9]. Most of residential Fallon is within 3 km of the hard metal facility, and much of Fallon is within 2 km of it. Thus, most Fallon residents potentially spend time daily within an environment of elevated levels of airborne tungsten.

Interestingly, urine samples of Fallon residents were significantly elevated in tungsten [27]. No linkage was concluded between elevated tungsten in Fallon residents and leukemia occurrence, in part because people from both the case and control populations showed elevated tungsten levels, dismissing tungsten as a discriminating factor for occurrence of leukemia. This inability to conclude linkage does not rule out linkage but rather reflects the difficulty of conclusively establishing linkage using the case-comparison study design [28].

In contrast to the roughly circular layout of Fallon, Sweet Home is relatively linear, stretching out along a single highway (Figure 4). The tungsten facility of Sweet Home is located just east of the center of town, on the northern side. Airborne tungsten loadings were elevated above background levels out to only 400 m away from the tungsten facility [20], a considerably shorter dispersal distance than the 3 km of Fallon. This could be explainable meteorologically: airborne heavy metals have been shown to correlate inversely with precipitation [29], and Sweet Home receives 10 times more rainfall than Fallon (Table 1). Little of residential Sweet Home lies within 400 m of the tungsten facility. Thus, few Sweet Home residents potentially spend time daily within an airborne environment with elevated levels of airborne tungsten. We know of no testing for tungsten in urine samples of Sweet Home residents to confirm exposure levels there.
3.4. Wind Patterns. Fallon typically experiences winds from the northeast, north, west, south, and southeast (Figure 5(a)). Given the central location of the hard metal facility in Fallon and these prevailing wind directions, much, if not most, of residential Fallon is downwind of the hard metal facility for at least some fraction of time at the annual scale. This should result in human exposure to elevated airborne tungsten levels for many, if not most, Fallon residents.

Sweet Home typically experiences winds from the northwest, west, southwest, and south (Figure 5(b)), or from the northwest and south (Figure 5(c)). Given the eastern location of the tungsten facility in Sweet Home and these prevailing wind directions, little of residential Sweet Home is downwind of the tungsten facility. This should result in little human exposure to elevated tungsten levels for Sweet Home residents.

4. Conclusions

As we have stated in prior work, it cannot be concluded from environmental data alone that elevated airborne tungsten...
causes childhood leukemia [9–13]. Such linkage requires direct biomedical research, which is at least supportable by the cooccurrence of exposure to airborne tungsten and a cluster of childhood leukemia [28, 30]. Tungsten has been evaluated for carcinogenicity, by itself [31, 32] as well as with other metals [33–36]. In general, this biomedical research has shown at least the possibility of linkage between exposure to tungsten and cancer.

Regardless of the toxicity of tungsten, this comparison of airborne tungsten and geography between Fallon and Sweet Home does lead to the following conclusion: the lack of excessive cancer in Sweet Home, which has an industrial tungsten facility as well as elevated levels of airborne tungsten, cannot logically be used to dismiss the possibility of airborne tungsten as a factor in the cluster of childhood leukemia in Fallon, which also has an industrial tungsten facility as well as elevated levels of airborne tungsten. The size distributions of airborne tungsten in each town are similar, but the relative sizes and locations of the tungsten facilities differ between Fallon and Sweet Home as do prevailing wind directions and annual precipitation amounts such that human exposure to airborne tungsten is probably higher in Fallon than in Sweet Home. Additional modeling of all variables affecting airborne loadings of heavy metals would be needed to legitimately compare human exposures to airborne tungsten in Fallon and Sweet Home. In any case, continued biomedical research on possible linkage of tungsten with leukemia is justified based on the cooccurrence of elevated airborne tungsten and a cluster of childhood leukemia in Fallon, Nevada.

Disclosure

P. R. Sheppard and M. L. Witten have provided documents, data, and declarations in Cases CV03-03482, Richard Jernee et al. versus Kinder Morgan Energy et al., and CV03-05326, Floyd Sands et al. versus Kinder Morgan Energy et al., Second Judicial District Court of Nevada, Washoe County, which are related to the childhood leukemia cluster of Fallon. In these cases, the law firm of Dunlap and Laxalt, representing the plaintiffs, with full disclosure to all defendants and their counselors, made an unsolicited donation of $15,000 to assist M. L. Witten and P. R. Sheppard in furthering their research, with a request that defendants provide similar donations. Neither M. L. Witten nor P. R. Sheppard have profited personally as a result of doing their research in Fallon or from providing material in these cases. B. J. Biernan and K. Rhodes declare that they have no conflict of interests.

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References


Research Article

Wider Action Plan and Multidisciplinary Approach Could Be a Winning Idea in Creation of Friendly Environment

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Herein, we proposed planning of wide transdisciplinary actions, which bring a solution for economic activity such as transportation, strongly related to pollution output with possible repercussions on climate change and public health. To solve logistics problem by introduction of common intermodal policy, and creation of more friendly transport solution, it is possible to obtain sustainable development, climate change prevention, government policy, and regulation which are all related to human health and creation of health-supportive environment. This approach permits environmental and biological monitoring same as economic results measurement by key performance indicators. This approach implementing emerging scientific knowledge in environmental health science such as genetic epidemiology aimed at understanding how genomic variation impacts phenotypic expression and how genes interact with the environment at the population level with subsequent translation into practical information for clinicians as well as for public health policy creation.

1. Introduction

Economic and industrial growth in the last century provoked the massive increase of air pollutants, resulting from more intense energy consumption and exhaust emissions from vehicles, with important global environmental consequences including climate change. Undoubtedly, increase of air pollutants same as global climate change will have multiple effects on human health especially on vulnerable populations such as children, the elderly, and the poor who are at increased risk from such events [1].

The contamination of air by organic and inorganic toxic pollutants same as exposure to motor vehicle emissions represents an important concern for possible long-term health effects [2–5]. Negative associations between traffic-related pollution and respiratory health have been underlined by different epidemiological studies on air pollution [6–15]. D’Amato et al. [16] reported observations that in the regions with high levels of vehicle traffic the interplay between climate change and the most abundant components of air pollutions (airborne particulate matter, nitrogen dioxide and ozone) alters the concentration and distribution of air pollutions and as consequence interferes with the seasonal presence of allergenic pollens in the atmosphere by prolonging this period with adversely effects on lung function in asthmatics. The air pollutants with well-established respiratory effects will potentially change as climate change [17, 18] and/or could be influenced by warming temperatures which can affect chemical reactions rates [19, 20]. Traditionally, climate change has been considered as an environmental rather than a health issue.

Quantification of the effects of climate change on health is needed on all levels (global, regional, and local) through enhanced monitoring of environmental health and one of the possible ways could be biomonitoring.
Biomonitoring of the exposure to complex mixtures such as polluted ambient air, vehicle exhaust, and smoke is a particular challenge since these exposures have many constituents in common and many people were exposed to more than one of these mixtures. It is well known that human biomonitoring comprises the determination of different validated biomarkers which are generally assigned to one of three classes: biomarkers of exposure, biomarkers of effect, and biomarkers of susceptibility. Their application in epidemiological studies has been proven. Most studies used random samples of citizens with mixed activities and exposure profiles, with intention to be representative of the whole population [21]. The intensity of exposure of the study subjects could be done with passive personal samplers as well as blood and urinary biomarkers and could be also compared with ambient, for example, benzene concentrations, measured by municipal monitoring stations [22].

As an example of good practice to be followed, a report on tobacco toxicants of the Institute of Medicine (USA) could be considered. Namely, reducing risk of disease by reducing exposure to tobacco toxicants is feasible and biological markers associated with tobacco-related disease could be used to offer guidance as to whether or not Potentially Reduced Exposure Products (PREPs) are likely to be risk-reducing [23].

This observation raised a simple question: if the same could be used to perform biomonitoring of populations at places of high traffic density, with higher exposition/air pollutions and could it be measured, obviously before and after introduction of friendly environment transport project with positive consequences on human health, climate change preparedness strategy as a part of public health programs?

Climate change and adverse environment are perceived as a health threat and the solutions are necessary by different type of actions. We focus on the health impact and possibility to propose public health strategy through energy consumption reduction, implementing new intermodal transportation chain. Stronghold for this approach underlined that framework for prevention includes incorporation of climate change actions into the 10 essential functions of public health as reported by Frumkin et al. [24].

The project idea was born during attempt to find a way how to connect South Italy (South Europe, Spain, and Portugal) to South East Europe/Balkan Peninsula countries in the most suitable way, with less air pollution, more traffic safety, and reduction of road congestion. This approach should be seen as immediate implementation of the European Union Common Transport Policy and enlargement of European Union on Balkan Peninsula countries, which are still out of EU and also to establish joined traffic management, as one of the most industrialized topic areas within transport research, with consequences for public policy issues related to government regulation, human health, and/or environment. Furthermore, this could be a way to create future strategy able to “burn out” timeline gap provoked by recent historical events and to prepare Balkan Countries for the future partnership giving to the Countries from this region a possible solution to help health promotion and building up environmental systems able to avoid the contamination (discussed with great interest at REACT—conference 2011 [25]).

2. Climate Change and Transportation

The greenhouse gas emission (GHG) in the decade up to 2008 for the EU27 decreased by 2,4%. Energy use, waste, manufacturing, construction, and agriculture were the areas where emissions decreased but at the same time emissions from energy industries, industrial processes, and transport were growing.

Figure 1 reported the most recent data published by EUROSTAT regarding the situation of GHG emissions by sector in decade up to 2008 [26].

The increase in emission of air pollutants and climate change due to economic and industrial growth has made air quality an important problem throughout the world. These emissions give rise to climate change with increased social costs (i.e., diseases), costs that do not have to be carried by the actual polluter. The GHG emissions in EU have been reduced in most sectors over the last 15 years, beside transportation which has shown a 25% increase (Figure 2) [27].

In order to come to terms with this, many European governments have to decide to take legislative actions. The level of GHG emission is to be reduced by 40% by 2020 and by 2030 the Swedish vehicle fleet is to be fully independent of fossil fuels. The social cost will have to be internalized and to achieve this carbon taxes and emissions trading schemes will be utilized [27, 28].

The company may choose between a number of measures in order to achieve a reduction. One measure commonly suggested is a shift in transport mode, from faster, more polluting mode such as road and air transport to slower and less polluting modes such as rail or sea transport developing proper logistics chain. A particularly interesting solution is an intermodal road-rail-short sea shipping solution. In this way, the flexibility and availability of truck transport is combined with low-cost, CO2 efficient, rail transport for the
longer part of the journey. Research has shown that, with this type of mode shift, CO₂ emission can be reduced by 20–50% or more depending on how the energy for the train part is produced [29, 30].

Climate change is a major threat to sustainable development. On the basis of Kyoto Protocol, EU15 has a collective target of 8% of reduction below levels chosen in a base year (mostly 1990) which had decreased by 2008 by 6.9%. After that, the EU27 has set a 20% reduction target to be achieved by 2020 [31].

Transport is the second largest source of emissions in the EU and it is the sector that has exhibited continuously growing emissions [26]. A task of the EU Sustainable Development Strategy is to achieve a balanced shift towards environmentally friendly transport modes which will bring about a sustainable transport and mobility system. This shift would certainly fall GHG emissions as well towards environmental friendly transport modes.

3. European Union Plans for the Region

EU plans for the Region are grouped in hard and soft measures; the hard measures are related to infrastructures and soft measures are harmonization and reforms (technical standards and border crossing procedures). The soft projects that are considerably affected by “regionalization” deal with the railways that could be solved by setting up Intergovernmental Working Group on Railway and Intermodal Policy.

The Working Group is to make an inventory of rail reforms and further recommend measures that ensure the regional integration and harmonization of the reforms for every country and to open access to transport infrastructure. Unfortunately, States have usually denied railways enterprises the freedom of a commercial business and this has to be changed. Different options are possible: some railways may focus entirely on their core business of operating trains. Others may choose to enter into partnership, for example, with road haulers or logistics companies and offer door to door intermodal services. Some may operate across Europe, while others may concentrate on local services. One thing in common of all railways in Region is that they must focus on what their customers want and how they can satisfy these needs. It is important to establish common traffic management which will focus on planning, monitoring, and controlling of traffic. The principal aim should be to maximize the effectiveness of the use of existing infrastructure, ensure reliable and safe operation of transport, address environmental goals, and ensure fair allocation of infrastructure space (road space, rail slots, etc.) among competing users [32].

Given the various confusions among stakeholders about the implication of the Carbon Pollution Reduction should serve to increase understanding of various effects of this initiative and possible multidisciplinary approaches regarding this theme.

4. Biomarkers and Adverse Human Exposure

For many years some cytogenetic alterations as biomarkers of genotoxic exposure have been used [33–38]. The fact that most established human carcinogens are genotoxic represents a relevant reason for using these assays [33]. In fact epidemiological studies strongly suggest that the high frequency of some of them is predictive of an increased risk of cancer [34, 38]. Gene polymorphisms are also able to modulate the human response to genotoxic insults [33, 39–43]. In fact any polymorphism that affects genes acting on metabolism or cellular response to DNA damage may alter individual sensitivity to genotoxic carcinogens.

From the 1950s mutagenicity testing became an important topic for geneticists who were well trained to recognize structural chromosome rearrangements (CA). Up today, different tests (SCE, MN, Comet Assay, etc.) were introduced which correlate at least with parts of metaphase chromosome aberration assays. The newest tests and approaches are faster and less laborious and do not require aberration assays. The newest tests and approaches are faster and less laborious and do not require aberration assays. The newest tests and approaches are faster and less laborious and do not require aberration assays. The newest tests and approaches are faster and less laborious and do not require aberration assays.

As exposure to environmental factors including tobacco smoke and diet may significantly affect the onset of most cancers [45], gene-environment interactions can modulate the outcome of such exposure influencing individual susceptibility to tumour initiation and development. Thus, genetic variability in metabolic activities related to some enzymatic pathways may partially explain individual susceptibility to cancer. The competition and interplay between different
metabolic pathways are expected to modulate the levels and pattern of the DNA adducts and consequently modify the risk of cancer development, and in several cases the polymorphic variants have been found to confer to the encoded enzymes higher or lower capacity to activate or detoxify the genotoxic compounds [37, 46].

Recently microRNAs (miRNAs; small noncoding RNAs) have been suggested to be important in maintaining the lung in a disease-free state through regulation of gene expression (epigenetics mechanisms); however little is known regarding whether environmental agents can induce such changes. Observation of Jardim et al. [47] reports that alteration of miRNA expression profiles by environmental pollutants such as diesel exhaust particles (DEPs) can modify cellular processes by regulation of gene expression, which may lead to disease pathogenesis. However, mechanisms of damage by DEP exposure to human respiratory health are only partially known, as reported by Li et al. [48]. The same authors confirm upregulation of Matrix-Metalloproteinase-1 (MMP-1) in response to DEPs in human bronchial epithelial (HBE) cells and suggest that human = 1607GG polymorphism is a susceptibility factor for high response [48].

More research for understanding of the interplay between genetic and environmental factors is necessary, as discussed by Comuzzie [49] regarding the challenge for applied genetic epidemiology and its relation on the information obtained by completion of Human Genome Project which is to put the human genome in context. This means not only to identify genes impact but also to know how they interact with the environment. Currently much of the effort in genetic epidemiology is largely focused on attempting to identify which genes influence which phenotypes, largely through genomewide efforts employing either case/control study designs utilizing association methods. While the identification of the key genes involved in the expression of a phenotype, particularly for those involved in mediating disease risk, is an important endeavour, it only represents a first step. It is highly doubtful that any gene will exert its effects completely in isolation but rather will have its action modulated by a wide range of other genetic, epigenetic, and also environmental factors. The identification of such environmental factors and the deciphering of how they impact the action of genes are a fundamental objective of genetic epidemiological analyses. Therefore, as the diversity, as well as shear amount, of genetic information continues to accumulate, the thoughtful definition and quantification of key environmental factors must also keep pace if we are to truly understand how the critical interaction between genes and environment gives rise to the phenotypic variation we observe at the population level [49].

5. What Could Be Done?

The idea is to create intermodal transport chain between Bari Logistic Center and Logistic Railways Terminals in Balkan Region avoiding the road traffic and reduction of CO₂ using short sea shipping by Ro/Ro vessels and block trains. One of the European Commission measures is to shift the balance between transport modes with focusing and promoting intermodal transport, type of transport strongly advocated due to its environmental concerns, safety reasons, and road congestions avoidance.

The first step is organization of railways practice in Bosnia and Herzegovina, Serbia, Romania, Montenegro, Croatia, and Bulgaria, mixing private and public consortia, which are going to be able to move merchandise from/to Southern Europe to/from Eastern Europe. It is necessary to create an Intergovernmental Working Group on Railways—new railway management model able to take care of the opportunities given by all existing European Programs on intermodal transport sector—which will include all countries interested in a project start up. The aim of EU policy is to reduce and also to eliminate technical and operational differences among national railway systems, with subsequently achieving harmonization in terms of technical specifications for infrastructure, signaling, telecommunications, and rolling stock taking care of certain operational rules [50, 51] creating common intermodal policy.

Furthermore, this idea could have operational implications in existence of more friendly transport solution, sustainable development, climate change prevention, government regulation, public education, and public policy issues related to human health by creation of health-supportive environment.

This is an integrated approach based on environmental and biological monitoring, including the analysis of biomarkers of exposure, early biological effects, and susceptibility that could be useful to evaluate global benefits (such as economics, logistics, transport, environmental, and/or climate impact) and would be the translation of emerging scientific knowledge in environmental health science into practical and useful information for clinical medicine as well as for public health policy.

6. Final Remarks

The influence of genetic polymorphisms of the genes encoding for detoxification enzymes on a series of biomarkers was demonstrated before [37].

Human variability, especially as it relates to polymorphisms in biotransformation enzymes, represents an important factor to consider in evaluating the effects of exposure to genotoxic substances, because polymorphisms are able to act on the individual susceptibility even to the neoplastic transformation [52].

Advances in molecular analysis give the possibilities for understanding the genetic contribution to phenotypic outcomes, same as to develop new and creative research designs and techniques to integrate the vast amount of biological information into models and careful measurement of the environment. This will, necessarily, have to be a multidisciplinary team science approach.

The contamination of air same as climate change is essentially a social problem and because of that it needs integral and coherent transport policy. The social implications of the transport need to be constantly and carefully monitored.

The starting point is to find sustainable transport and welcome the development of infrastructure changing as
Figure 3: Schematic presentation of project idea. Starting from logistic problem, passing through possible solution-introduction of intermodal transport, problem solution could be achieved with improvement on climate change, security, and safety with positive effects on public health.

A policy instrument to contain and reduce congestion, and reduce environmental impacts. It is well reported by Kreutzberger et al. [53] that the environmental performance of intermodal transport is substantially better than that of unimodal road transport when looking at every use and GHG emission and this is even more outspoken when also local emissions, accidents, congestion, and noise are integrated. As regards of the automatic link between economic growth and growth in freight transport, the solution is not in reduction of transport but in redistribution between modes. This is a main reason and strength of a project idea which could bring a success. Furthermore, in this case we are not only talking about redistribution between modes [54] of transport but also we are implementing a new corridor. Enlargement of the European Union is set to trigger larger exchanges of goods and so need for additional investments in transport infrastructures. It is well known that south-east Europe transport system distinguishes itself by extremely fragmented transport. Italy, especially South Italy, with its geographical position, cultural, political, humanitarian, and historical connections could have prestige and favorable role between European Union and Balkans. Implementation of legal regulations under supervision could produce different positive consequences on health, transport, environment, climate, and so forth.

Environmental pollution is reaching worrying proportion worldwide and solution probably could be in different small changes of lifestyle habits which, all together, will be able to produce reduction of potentially toxicants, money waste, and improvement of environmental with improvement of health and life quality.

We can find a good example in “multifactorial” diseases. “Multifactorial” recognizes that these disorders are the result of both environmental and genetic factors and does prejudge the relative role of either category. Namely, in this type of diseases when conditions are favorable, that is, different mutations and/or polymorphisms of susceptibility together with adverse environment conditions, a pathological situation is observed. However if involved genes are going to be considered singularly, no one will be able to produce pathology, but with contribution given by every gene, the interaction between them, and environment we have to deal with illnesses.

Finally we proposed in Figure 3 wide transdisciplinary actions of project idea, which brings a solution for economic activity such as transportation, strongly related to pollution output with possible repercussions on climate change and public health.

So, if we consider our planet as “living organism” and our action as expression of genes, then individually small actions in different fields could be extremely potent and benefits could be obtained to us and future generations.

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Research Article

Effects of Three Types of Oil Dispersants on Biodegradation of Dispersed Crude Oil in Water Surrounding Two Persian Gulf Provinces

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Objective. To determine the most effective and biodegradable dispersant of spilled oil in water surrounding two Persian Gulf provinces. Methods. This study compared the effects of three dispersants, Pars 1, Pars 2, and Gamlen OD4000 on removal of oil in two Persian Gulf provinces’ water. Overall, 16 stations were selected. Using the Well method, the growth rate of isolated bacteria and fungi was identified. To specify the growth rate of microorganisms and their usage of oil in the presence of the above-mentioned dispersants, as exclusive sources of carbon, the bacteria were grown in culture medium for 28 days at 120 rpm, 30°C, and their optical density was measured by spectrophotometry. Then, we tested biological oxygen demand (BOD) and chemical oxygen demand (COD) in microorganisms. Results. The highest growth rate was documented for the growth of microorganisms on either Pars 1 or Pars 2 dispersants or their mixtures with oil. However, the culture having microorganisms grown on Pars 1 had higher BOD and COD than the other two dispersants (9200 and 16800 versus 500 and 960, P < 0.05). Mixture of oil and Pars 2 as well as oil and Pars 1 dispersants showed the highest BODs and CODs, respectively. In the Bahregan province, microorganisms grown on Pars 2 had maximum amount of BOD and COD in comparison with Pars 1 and Gamlen dispersants (7100 and 15200 versus 6000 and 10560, P < 0.05). Conclusion. Pars 1 and Pars 2 were the most effective dispersants with highest degradability comparing Gamlen. In each region, the most suitable compound for removing oil spill from offshores with least secondary contamination should be investigated.

1. Introduction

The main causes of oil pollution in the oceans are extraction of oil, transportation with ballast water release and tanker accidents, and also war-related incidents [1]. Unfortunately, such incidents are not uncommon. Land and offshore oil wells also can be a source of oil spills into ocean water. Oil spills from such accidents may quickly spread over many square miles of water surface. The spills are particularly destructive for local wildlife and plant life when they get close to shorelines. They also damage boats, fishing gear, and harbor installations and greatly diminish the value of the shore as recreational resources [2–4].

The use of dispersants in nearshore areas is expected to increase the exposure of aquatic organisms to petroleum [5]. If not treated, crude oil spills would require long period of time to naturally biodegrade; it nearly takes 22 years for complete biodegradation of one kilogram of crude oil by natural processes [6].

Considering the lack of ability of any bacterial strain for complete catabolism and biodegradation of crude oil, finding appropriate strains is necessary. Even microorganisms which...
are consumers of non-hydrocarbonate components occasionally play important roles in removal of crude oil from the environment [7].

Many methods have been used to remove oil spills from water including physical removal of crude oil, chemical remediation of the spills using dispersants and so-called “sinking agents,” and, in some cases, intentionally burning floating petroleum slicks. Using chemical dispersants as an oil spill countermeasure is the most frequently employed clean-up method because such liquids can be readily applied to large oil spills, and also this method is generally more cost effective than physical remediation methods [3, 4].

Furthermore, the exclusive property of these dispersants to make oil spills dispersed into water will enhance the biodegradability of crude oil due to the increased exposed surface of the spills to such agents [8].

Chemical dispersion of an oil slick increases the petroleum toxicity. When the meteorological conditions induce the dispersion of the oil slick such as wave, the application of dispersant does not rise the petroleum toxicity [5]. The significant differences between chemically dispersed oil and water-soluble fraction of oil highlight the environmental risk to disperse an oil slick. The lack of significance between chemically and mechanically dispersed oil suggests that dispersant application is no more toxic than the natural dispersion of the oil slick [9].

Dispersants contain surfactants, which are surface-active agents with molecules composed of groups of opposing polarity and solubility; that is, surfactants usually have both an oil-soluble hydrocarbon chain and a water-soluble group. The synthetic surfactants can be anionic, cationic, nonionic, or amphoteric; however, only anionic or nonionic surfactants are utilized as crude oil dispersants. Surfactant mixtures often include other chemical agents, such as solvents, which enhance the dispersing capability of the surfactant [10].

Chemical surfactants are amphiphilic compounds which can reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids and increase the solubility and mobility of hydrophobic or insoluble organic compounds [11–13].

Chemical surfactants can increase the pseudosolubility of petroleum components in water [14, 15]. They are effective in reducing the interfacial tensions of oil and water in situ, and they can also reduce the oil viscosity and remove water from the oil prior to processing [16, 17].

Nevertheless, not all surfactant compositions are efficient in dispersing spilled oil products, and many of the effective ones have the drawbacks of being toxic and/or not biodegradable [4]. Biodegradability of such components is absolutely crucial; otherwise, they get accumulated in the environment and make the secondary cause of water contamination. Modern-day dispersants are much less toxic to sea water than those used in the past. However, concern still exists on their possible toxic effects, on fresh water organisms, especially if dispersants are used near shore waters [18].

This study was conducted to determine the most effective and biodegradable dispersant of spilled oil in water surrounding two Persian Gulf provinces.

2. Methods and Materials

We selected two provinces in Persian Gulf because of their location in one of the biggest offshore oil drilling rig and high traffic density of oil vessels in the sea lanes of Persian Gulf; Siri and Bahregan provinces were studied because of their numerous shorelines contaminated by oil spills. We compared the effects of the dispersants produced by Iranian Offshore Oil Company, that is, Pars 1 Pars 2 in comparison with Gamlen, which is actually used in the Persian Gulf water. Biodegradability of Gamlen and its effects on dispersing of oil had already been studied [11, 19].

The culture used in the investigation was originally isolated from 16 sampling stations located at different longitude and latitude in the Siri and Bahregan province offshore (Table 4).

Microorganisms were isolated through common microbiological experiments under the sterile condition. They were cultured in the presence of Pars 1, Pars 2, and Gamlen separately and also the combination of each with oil at a dispersant-to-oil ratio of 1/20 [10, 20]. Dispersants were the only source of carbon in the culture. The ability of bacteria and fungi to grow at the sides of wells was assayed using the Well method and their growth rate was measured through optical density reading.

In this regard, isolated microorganisms, which were able to grow at the side of wells, were individually cultured overnight. 100 mL of manual culture media ((concentration in 1/mg): KH2PO4 (170), K2HPO4 (435), Na2HPO4·7H2O (668), NH4Cl (850), MgSO4·7H2O (22·5), CaCl2·2H2O (27·5), and FeCl3 (0·25)) and 2 mL of fresh overnight culture of each microorganisms were poured into six 500 mL flasks. Dispersants as an exclusive source of carbon were added to each flask as follows: flask 1: Pars 1, flask 2: Pars 2, flask 3: Gamlen, flask 4: Pars 1 and oil, flask 5: Pars 2 and oil, flask 6: Gamlen and oil.

It should be noted that the series of flasks containing both dispersant and oil was set up by preparing 1 : 20 dilution of the dispersant/crude oil [10]. Six control flasks contained sterile media, dispersants, and/or crude oil. All flasks were incubated at 30°C shaking at 120 rpm for 28 days. In different time intervals (24, 48, and 72 hours and 1, 2, 3, and 4 weeks), the optical density of each sample was measured using spectrophotometer at wave length of 600 nm. Oil components and dispersant were isolated from each sample prior to oxygen demand (OD) reading using Hexane Normal [21].

In order to identify the biodegradation of above-mentioned dispersants and their mixture with oil in the sampling stations, the BOD and the COD of each sample were measured in the presence of total microorganisms [22, 23]. The procedure was as follows: 1 mL of water obtained from each station was inoculated into marine broth in 8 screwed cap tubes and one tube was kept as control. Marine broth which is an enriched bacterial medium was used for enhanced growth of all type of microorganisms. After incubating the tubes at 37°C for the period of 48–72 hours, all culture media of 8 tubes containing the grown microorganisms were put together in nutrient broth.
media and were cultured over night. Therefore, a culture media containing all microorganisms obtained from the sampling stations was prepared. Then, 1 mL of bacterial suspension obtained from total microorganisms’ culture was inoculated to each flask containing 100 mL of manual media. Furthermore, the component was singly added to the series of flasks so that each flask contained only one type of dispersant or its mixture with oil as follows: 1 mL crude oil, 1 mL Pars 1, 1 mL Gamlen, 1 mL Pars 2, 1 mL mixture of crude oil and Pars 1, 1 mL mixture of crude oil and Pars 2, 1 mL mixture of crude oil and Gamlen, and their BOD and COD were measured after 5 days using the standard method [24].

The standard microbiological procedures were used to identify the species of the bacterium and fungus microorganisms.

2.1. Statistical Analysis. The obtained data was analyzed by the Statistical Package for Social Sciences software version 15.0 (SPSS Inc, Chicago, IL, USA) using analysis of variance (ANOVA) and post hoc Tukey statistical tests.

3. Results

Based on standard microbiological procedures, 4 genera of bacteria and 3 genera of fungus in Siri province and 4 genera of bacterium and 2 genera of fungus in Bahregan province were identified.

3.1. Results Obtained from the Well Method. The ability of bacteria and fungi to grow in the presence of dispersants individually or mixture of each with crude oil is presented in Table 1 and Figure 1.

The highest number of bacteria and fungi in Siri Province were those cultured in the presence of Pars 1, Pars 2 or separate mixture of each with crude oil, whereas in Bahregan Province, the bacteria around Pars 1 and Pars 2, had better growth rate compared with Gamlen.

3.2. Biomass Analysis of Bacterial Culture Using the Optical Density Reading. In Siri province, the microorganisms isolated from the sampling stations, which had the ability to grow at the side of wells in the Well method, were cultured 28 days for the purpose of biomass analysis. The bacteria and fungi were grown for 28 days, and their optical density was measured in different time intervals. The OD reading showed that the highest growth occurred in the presence of either Pars 1 or Pars 2 or their separate mixture with crude oil.

The results of ANOVA and post hoc Turkey statistical tests are shown in Table 2.

As shown in Table 2, in Siri province significant differences \( (P = 0.006) \) were documented in the effects of isolated microorganisms (4 bacteria and three fungi) on different dispersants (Pars 1, Pars 2, and the combination of Gamlen dispersant with crude petroleum) after 24 hours.

The comparison of the mean growth rate using hoc Tukey test exhibited that there is meaningful differences between Pars 1 and Gamlen dispersants \( (P = 0.046) \) and also between Gamlen and combination of crude oil with Pars 1 \( (P = 0.005) \). In other words, the effect of microorganisms on Pars 1 dispersant is more than that on Gamlen dispersant.

This finding is in agreement with the result obtained from the Well method experiment.

The results of ANOVA test on day 28 did not show significant difference in effects of microorganisms among each dispersant separately or their combination with crude oil.

The results of ANOVA test on day 28 \( (P \leq 0.755) \) showed that there is no meaningful differences in effects of microorganisms among each dispersant separately or their combination with crude oil.
Table 1: Frequency of microorganisms grown at the side of wells in the Well method.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Frequency of fungi</th>
<th>Frequency of bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siri province</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pars 1 dispersant</td>
<td>10</td>
<td>43</td>
</tr>
<tr>
<td>Pars 2 dispersant</td>
<td>8</td>
<td>31</td>
</tr>
<tr>
<td>Gamlen dispersant</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Pars 1 + crude oil</td>
<td>24</td>
<td>95</td>
</tr>
<tr>
<td>Pars 2 + crude oil</td>
<td>25</td>
<td>68</td>
</tr>
<tr>
<td>Gamlen + Petroleum</td>
<td>24</td>
<td>65</td>
</tr>
<tr>
<td>Bahregan province</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pars 1 dispersant</td>
<td>20</td>
<td>91</td>
</tr>
<tr>
<td>Pars 2 dispersant</td>
<td>18</td>
<td>89</td>
</tr>
<tr>
<td>Gamlen dispersant</td>
<td>12</td>
<td>84</td>
</tr>
<tr>
<td>Pars 1 + crude oil</td>
<td>14</td>
<td>81</td>
</tr>
<tr>
<td>Pars 2 + crude oil</td>
<td>11</td>
<td>88</td>
</tr>
<tr>
<td>Gamlen + Petroleum</td>
<td>4</td>
<td>33</td>
</tr>
</tbody>
</table>

Table 2: The effect of isolated microorganisms on Hydrocarbonate compounds in 24 hours.

<table>
<thead>
<tr>
<th>Compounds of hydrocarbon</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pars 1 dispersant</td>
<td>0.126</td>
<td>0.082</td>
</tr>
<tr>
<td>Pars 2 dispersant</td>
<td>0.055</td>
<td>0.049</td>
</tr>
<tr>
<td>Gamlen dispersant</td>
<td>0.011</td>
<td>0.004</td>
</tr>
<tr>
<td>Crude oil</td>
<td>0.072</td>
<td>0.046</td>
</tr>
<tr>
<td>Pars 1 dispersant + petroleum</td>
<td>0.156</td>
<td>0.098</td>
</tr>
<tr>
<td>Pars 2 dispersant + petroleum</td>
<td>0.104</td>
<td>0.087</td>
</tr>
<tr>
<td>Gamlen dispersant + petroleum</td>
<td>0.115</td>
<td>0.067</td>
</tr>
</tbody>
</table>

Coefficient $F = 3.53, P = 0.006$, SD: standard deviation.

The optical density of one sample of bacterial and fungal cultures with the highest absorbance during 28 days in Siri province is depicted in Figures 2(a) and 2(b).

As shown in Figure 2(a), on the day 28, the highest growth rate of *Aureobasidium* spp. fungus in Siri province was observed in the presence of Pars 2 dispersant and the combination of Pars 2 dispersant with crude oil. The growth pick occurred in the first 24 hours in the presence of combination of Pars 2 dispersant with crude oil. However, the growth rate of microorganisms in the presence of Pars 1 dispersant was also noticeable.

As shown on Figure 2(b), on day 28, the highest growth rate of *Pseudomonas* spp. bacteria in Siri province was high when they were grown in the presence of combination Pars 2 dispersant with crude oil and. On day 14, high growth rate of the microorganism was observed in the presence of combination of Pars 1 dispersant with crude oil.

In Bahregan, province, the absorbance rate of samples during 24, 48, 72 hours, and 1–4 weeks was measured with spectrograph in 600 nm wave length. Moreover, according to Figures 3(a), 3(b), 3(c), and 3(d) that show the growth rate in 4 bacteria of Bahregan, the maximum rate was when they were grown in the presence of Pars 1 and Pars 2 dispersants.

3.3. Results of BOD-COD Tests. The results from BOD and COD analyses are shown in Table 3; the BOD and COD levels in culture having only Siri province crude oil were very low, but, when treated by dispersants, the levels increased. However, as the results show among different combinations of crude oil and dispersants in Siri province, the mixture of crude oil and Pars 2 had the highest BOD and COD followed by the mixture of crude oil and Pars 1. Moreover, among the three different dispersants under study, Pars 1 had the highest BOD and COD. However, in Bahregan Province the maximum level of BOD was devoted to Pars 2, Pars 1 and Gamlen, respectively. The combination of crude oil and
dispersants had similar effect with Pars 1 and Pars 2, and it was more than the combination of Gamlen with crude oil.

The highest COD was related to Pars 2, Gamlen, and Pars 1, respectively. Moreover, the highest amount of COD is related to combination of Pars 2 with oil.

The overall results show that Pars 1 and Pars 2 dispersants produced by the Iranian Offshore Oil Company were more effective than Gamlen dispersant in Siri and Bahregan provinces.

4. Discussion

In this study, we compared the effectiveness of three dispersants on removal of oil spills; since the highest numbers of microorganisms grown around wells containing Pars 1, Pars 2 and also their separate mixtures with crude oil, our findings suggest that both Pars 1 and Pars 2 dispersants are more effective in biodegradation of crude oil. Furthermore, they have more biodegradability and bioadaptability properties compared with the Gamlen dispersant. We found that by
growth rate was found in the presence of Pars 1 and Pars dispersants or their combination with Siri province crude oil. show-able growth in the presence of the other dispersants, respectively, showed higher degradability and growth rate. However, in 2 other bacteria which are related to Pseudomonas spp and Bacillus genus (7-P and 8-E), the highest growth rate is when Pars 1 and Pars 2 are the only sources of carbon in the environment. In 7-P bacterium, the highest growth rate was observed in the presence of Pars 1 dispersant after one week. 8-E bacterium had the highest growth in the first week in the presence of Pars 1 dispersant and in 4th the week with presence of combination of Pars 1 and crude oil. Moreover, 5-C and 1-E showed the highest growth rate after four weeks in the presence of Pars 2 dispersant.

These findings confirm that Pars 1 dispersant has more adaptability to both province ecosystems, and also they have more ability in biodegradation of crude oil compared with the other two dispersants. There was no significant differences in the effect of microorganisms on each dispersant and also on their combination with crude oil after 28 days. However, since the entered material to the ecosystem needs to be degraded fast, Pars 1 dispersant which shows more degradability in the first 24 hours comparing other dispersants, is more adaptable to the environment.

In Siri province, The growth diagrams of *Pseudomonas* spp. bacteria in 4 weeks showed the highest growth rate of bacteria to the great extent in the presence of Pars 1 dispersant and slightly lower extent in the presence of Pars 2 dispersant. The growth peak was seen on day 14 in the presence of combination of Pars 1 dispersant and crude oil. The growth curve of *Aureobasidium* spp. fungus shows that on day 28, the highest optical density is observed when the microorganism is cultured in the presence of Pars 2 and its mixture with crude oil; also the growth peak occurred in the presence of the aforementioned mixture in the first 24 hours. However, the microorganisms had also enhanced growth in the presence of Pars 1 dispersant.

The optical density of microorganism cultures containing dispersants is indicating the usage of these components as the sole carbon source which leads to microorganism growth and catabolism of the carbohydrate [11, 25]. Therefore, the result of the OD reading and the Well method experiments show that Pars 1 and Pars 2 are more effective in biodegradation of crude oil of both provinces, also they are more biodegradable than Gamlen dispersant. Overall,

<table>
<thead>
<tr>
<th>Table 3: The measurements of BOD and COD (mg/mL).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil + Gamlen</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>BOD₃ test (mg/mL)</td>
</tr>
<tr>
<td>COD test (mg/mL)</td>
</tr>
<tr>
<td>Bahregan province</td>
</tr>
<tr>
<td>BOD₃ test (mg/mL)</td>
</tr>
<tr>
<td>COD test (mg/mL)</td>
</tr>
</tbody>
</table>

BOD: biological oxygen demand; COD: chemical oxygen demand.

<table>
<thead>
<tr>
<th>Table 4: Longitude and latitude coordinates of the sampling stations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Station number</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Siri province</td>
</tr>
<tr>
<td>(1)</td>
</tr>
<tr>
<td>(2)</td>
</tr>
<tr>
<td>(3)</td>
</tr>
<tr>
<td>(4)</td>
</tr>
<tr>
<td>(5)</td>
</tr>
<tr>
<td>(6)</td>
</tr>
<tr>
<td>(7)</td>
</tr>
<tr>
<td>(8)</td>
</tr>
<tr>
<td>Bahregan province</td>
</tr>
<tr>
<td>(1)</td>
</tr>
<tr>
<td>(2)</td>
</tr>
<tr>
<td>(3)</td>
</tr>
<tr>
<td>(4)</td>
</tr>
<tr>
<td>(5)</td>
</tr>
<tr>
<td>(6)</td>
</tr>
<tr>
<td>(7)</td>
</tr>
<tr>
<td>(8)</td>
</tr>
</tbody>
</table>

using the Well method experiment, the highest number of isolated bacteria and fungi was able to grow at the side of wells containing Pars 1 dispersant. The growth index represents the mass of microorganisms at the side of wells containing dispersants which indicates the ability of microorganisms to use crude oil and dispersant components [20]. Therefore, microorganisms grew around the wells are considered as petroleum-degrading microorganisms. In this agreement, the highest optical density was related to the bacterial culture containing above-mentioned dispersants as the exclusive carbon source.

The result of statistical calculations on isolated bacteria (4 genera) and fungi (3 genera) in Siri province showed that in the first 24 hours, noticeable growth has occurred in the presence of Pars 1 dispersant as well as its combination with crude oil showing significant difference compared to the growth of the same organisms in the presence of the other dispersants or their combination with Siri province crude oil. In Bahregan province, in all conditions the maximum growth rate was found in the presence of Pars 1 and Pars 2 in the environment. In 4 bacteria of Bahregan province, combination of crude oil with 2 bacteria of 5-E and 1-E which are related to *Flavobacterium* spp. and *Enterobacter* spp., respectively, showed higher degradability and growth rate.
these findings suggest that Pars 1 and Pars 2 are more bioadaptable for both province offshores.

In agreement with results obtained from optical density reading and the Well method experiment, microorganism culture containing Pars 1 showed the highest level of BOD and COD. BOD is an indicator of biodegradation of organic components in water. BOD is measured by the amount of required oxygen for bacteria to metabolize organic components. The flasks are kept at 20°C for 5 days and the amount of dissolved oxygen is determined by chemical procedures. The BOD test identifies the approximate amount of required oxygen for biological oxidation of contaminated water, surplus water, and sewages. This is the only experiments determining the amount of required oxygen for bacteria in order to catabolize the organic components. Therefore, the higher BOD shows the increased amount of consumed oxygen which is consequently indicating the enhanced bacterial activity [24].

The COD value indicates the amount of oxygen needed to chemically oxidize organic compounds present in wastewater and adjacent to oxidizing material. In fact, chemical oxygen demand determines the amount of organic compound present in the sample which has the ability to be oxidized by a strong chemical oxidizing agent [24].

BOD and COD tests are well-known methods for assessment of biodegradability of organic materials such as surfactants; for instance, in a study in 1976, the percentage of biodegradation of 123 organic compounds was assayed [23].

Previous studies showed that none of the bacterial species are able to catabolize all the components of crude oil, and its complete biodegradation depends on the presence of various bacterial species and microorganisms. Even microorganisms which are consumers of non-hydrocarbonate compounds can play important role in biodegradation of crude oil [7]. Thus, in the present study, we measured the BOD and the COD of all microorganism cultures, which were originally isolated from sampling stations in the Persian Gulf in the presence of three dispersants and their mixtures with crude oil and also crude oil alone.

In this study, the highest BOD and COD in Siri province were related to culture containing Pars 1 in comparison with the two other dispersants studied.

Likewise, BOD-COD test performed on different combinations of dispersants and crude oil showed highest score for the combination of Pars 1 and crude oil and secondly to the mixture of Pars 2 and crude oil. Moreover, in Bahregan province the maximum BOD and COD devoted to Pars 2 dispersant. These findings suggest that microorganisms with the presence of these compounds require the highest amount of oxygen for their activities including the biodegradation of such components. Furthermore, in oxidation and degradation reactions, in presence of oxidizing agents, the highest amount of chemical oxygen is demanded; therefore; Pars 1, mixture of Pars 2 and crude oil, and also mixture of Pars 1 and crude oil hold more degradability properties compared to the mixture of Gamlen and crude oil. In fact, Pars 1 and Pars 2 increased biodegradability of crude oil more than the Gamlen dispersant. Since Pars 1 showed more degradability compared with the other two dispersants, the biodadaptability of this dispersant is high enough, so that it does not get accumulated in the region and does not make the environment contaminated.

5. Conclusion

This study revealed that Pars 1 and Pars 2 dispersants are more biodegradable than Gamlen and have more effectiveness in biodegradation of crude oil. These findings suggest that, in each region, the most suitable compound for removing oil spill from offshores with least secondary contamination should be investigated.

Acknowledgments

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References

and results from the Exxon Valdez oil spill in Alaska,"  


Research Article

Environmental Impact Assessment of the Industrial Estate Development Plan with the Geographical Information System and Matrix Methods

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Background. The purpose of this study is environmental impact assessment of the industrial estate development planning. Methods. This cross-sectional study was conducted in 2010 in Isfahan province, Iran. GIS and matrix methods were applied. Data analysis was done to identify the current situation of the region, zoning vulnerable areas, and scoping the region. Quantitative evaluation was done by using matrix of Wooten and Rau. Results. The net score for impact of industrial units operation on air quality of the project area was \((-3)\). According to the transition of industrial estate pollutants, residential places located in the radius of 2500 meters of the city were expected to be affected more. The net score for impact of construction of industrial units on plant species of the project area was \((-2)\). Environmental protected areas were not affected by the air and soil pollutants because of their distance from industrial estate. Conclusion. Positive effects of project activities outweigh the drawbacks and the sum scores allocated to the project activities on environmental factor was \((+37)\). Totally it does not have detrimental effects on the environment and residential neighborhood. EIA should be considered as an anticipatory, participatory environmental management tool before determining a plan application.

1. Introduction

The existing tendency of industrialization and urbanization in developing countries has an enormous impact on natural and man-made environments. Pollution sources increase with the development of cities and cause contamination of air, water, and soil. Lack of urban environmental planning and management strategies has led to better concern for upcoming urban expansion [1].

Unprecedented growing rates of global human population and urban development make tremendous stress on local, regional, and global air and water quality. A necessity to better understanding of the factors that mediate the interactions between urbanization and variations of environmental quality exists [2].

Land use modification, urbanization, and infrastructure developments specifically could destruct the natural environments and are threatening the biodiversity. Tools and measures must be adapted to evaluate and remedy the potential effects on biodiversity caused by human activities and developments. Within physical planning, environmental impact assessment (EIA) plays important roles in the prediction and assessment of biodiversity-related impacts from planned developments [3].
EIA is one of the main legislative tools recognized to reduce an anthropogenic impact on the environment. EIA can be defined as “a process by which information about the environmental effects of a project is collected, both by the developer and from other sources, and taken into account by the relevant decision-making body before a decision is given on whether the development should go ahead.” [4].

The purpose of EIA is to ensure that the environmental effects of a proposed development are fully considered, together with its economic or social benefits. This should be considered before the planning application would be determined. EIA is thus an anticipatory, participatory environmental management tool.

The extensive understanding of EIA as an anticipatory environmental management tool has made a significant consideration over the extent to which it is achieving its purposes. This has been measured in terms of EIA “effectiveness,” especially as discussion has moved away from issues of procedural operation to the more practical goals of EIA and its place in more comprehensive decision-making situations [5].

Geographical information systems (GISs) bring the opportunity to enhance predictable evaluation techniques (e.g., matrix-based assessments). It acts as graphic mediators of spatial knowledge and by providing an effective tool for the spatial and temporal analysis of environmental impacts. GIS has the potential to increase the objectivity and accuracy of the assessment, to improve both the understanding of environmental and planning concerns and the distribution of information. Therefore, it may help to develop the effectiveness of strategic environmental assessment practice [6].

For monitoring industrial pollution in the case of developing countries, the design of policy instruments is a demanding task. In principle, the regulator has a collection of physical, legal, financial, and other tools. However, existence of a great number of small-scale industries and informal region pollution sources, requiring knowledge, funds, technology, and skills to treat their effluent, leads to failure [7].

At the present time, due to the inappropriate expansion of industries in Iran, similar to other developing countries, environmental attitudes for suitable protection of environment are vital for next generations, and it has attracted authorities’ attention. In this regard, the government has attempted to establish and to develop different industrial estates in various parts of the country for managing industrial activities to control the environmental pollution [8].

The environmental impacts of projects or actions generally include a comprehensive range of impacts. All these impacts vary in magnitude, as well as in their beneficial or adverse organization [9].

According to the industrial estates company’s policy in Iran, planning the industrial units follow specific patterns and in each estate separated sites have been predicted for different industries. Therefore, each industry could be a potential source of solid, liquid, and gaseous emissions and their effects on humans, natural flora, air, soil, water sources, climate conditions, cultural heritage, and valuable materials should be evaluated.

The purpose of this study is to establish EIA for an industrial estate development planning in Iran by using the GIS and matrix methods.

2. Materials and Methods

This cross-sectional study was conducted in 2010, in Isfahan province, in central Iran. The following methods were used for EIA.

2.1. GIS Assessment Method. Environmental evaluation of Koohpayeh industrial estate by using GIS was conducted by the following processes.

2.1.1. Identifying Effective Factors in Environmental Degradation. Including climate, geology, hydrology data, and some degradation factors in the region such as its location, different types of pollutants, land use, and ecological data.

2.1.2. Collecting and Entering Data. The collection of information on the site and surroundings of the proposed development (“baseline” information) is essential in EIA, as in the implementation of any proposed development.

2.1.3. Data Analysis. Required data for analyzing maps of different organizations was gathered with scale of 1:50000 and using the Universal Transverse Mercator (UTM) system, and they were given digits with ARC GIS software. In analyzing steps, data analysis was done by using existing operators to identify the current situation of the region, zoning vulnerable areas, and scoping the region, which is affected by pollutants. For this purpose, overlay method and analysis of ground water was used.

To perform zoning, considered parameters were selected and then they were scored by expert evaluators. Thereafter, classified layer zones were categorized.

2.2. Evaluation with Quantitative Method by Using the Matrix. Quantitative evaluation method was done by using the matrix of Rau and Wooten [9], that is, the other format of Leopold Matrix (1).

\[
\text{Net score for impact} = \text{magnitude of effect} \times (\text{importance of effect}). \quad (1)
\]

In each project, the effect magnitude of activities is defined based on environmental parameters with classifying each group of pollutants; for example, it is defined based on technical and scientific principles for determining effect magnitude of each group. The scope for importance of effect is similar for all of the impacts. In this study, the range of importance of effect is defined with the numbers of 0 to 5 as it presented in Table 4.

2.3. District of the Study Area. In this study, development planning of the industrial estate, located in the Isfahan province, central of Iran, was evaluated. The current area
of the industrial estate is 150 hectares (Figure 1, dark color part), and its extent development planning is 350 hectares. The development plan is included various types of industries such as food, chemical, ceramic industries, thermal and sound insulation, and other manufacturing industries (Figure 1).

3. Results

The entries in matrix represent not only an indication of the areas impacted by each action, but also serve as a measure of the impact’s extent. Table 1 provides an illustration of the basic structure of the matrix method approach, namely, a matrix in which each proposed action (or its separate components) is identified as a column of the matrix and the environmental conditions or impacted areas are identified as the rows of the matrix.

3.1. EIA for Gaseous and Particulate Pollutants via Matrix

3.1.1. Qualitative Analysis. Based on daily meteorological data in synoptic station of Naein city in a one year period (2010), the minimum and maximum speed of prevailing wind were 0 and 15 m/s, respectively. Moreover, most days in a year have a mild air flow. So, Koohpayeh region is in class C of atmospheric stability classes and the region atmosphere is slightly unstable. Therefore, the particulate and gaseous pollutants will become diluted and their negative effects would reduce. However, the wind rose of the region (Figure 2) shows that the prevailing wind in this industrial estate has east-west direction and vice versa with 21% of region wind rose. There is no residential area in downstream, and air pollutants have enough opportunity for becoming diluted in the environment. Instability air in industrial estate location cause releasing the emissions and it increases the concentration of air pollutants in comparison with background air.

3.1.2. Quantitative Analysis. Given the mentioned conditions, the importance of particulate and gaseous pollutants on this industrial estate air quality is very low with the score of 1 (Table 1). Moreover, considering the atmospheric stability, the magnitude of effect for C stability class is $-3$ (Table 5). Therefore, as shown in Table 1, cell (4, 11), the net score for impact of “industrial units operation” on “air quality” of the project area is equal to $-3$ [$1 \times (-3) = -3$].

The magnitude effect of particulate and gaseous pollutants on air quality based on atmospheric stability classes is determined in Table 5.

3.2. Air Pollution Assessment through GIS. Considering the highest percentage wind speed of 2–5 m/s in the study area with an average speed of 3 m/s, the height of 25 m for the most elevated stack in the estate, and using Gaussian model, pollutants concentration in various distances from the estate is indicated in Table 2.

According to the transition of industrial estate pollutants, residential places located in the radius of 2500 meters of the city would be affected more (Figure 3).

3.3. Gaseous and Particulate Pollutants Effects on Plant Species. The status of pastures has been selected as a criterion of evaluating pollutants effects on plants. Due to severe destruction of soil and vegetation in the pastures, five classes were considered for rating. For this purpose, rangeland vegetation percentage method is provided by US Range service.

In this method, current rangeland composition vegetation of increaser and decreaser plants are calculated in climax stage, and their statuses will be determined by using 5 class-scales in Table 6.
### Table 1: Matrix for EIA of the industrial estate.

<table>
<thead>
<tr>
<th>Project Activities</th>
<th>Soil and Earth</th>
<th>Ground water quantity and quality</th>
<th>Flood</th>
<th>Air quality</th>
<th>Noise</th>
<th>Plant and animal species</th>
<th>Occupation</th>
<th>Housing, education, and welfare</th>
<th>Emigration</th>
<th>Health and safety</th>
<th>Total Factor Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavation and embankment</td>
<td>1</td>
<td>−2(2)</td>
<td>0</td>
<td>−1(2)</td>
<td>−1(1)</td>
<td>−2(1)</td>
<td>1(3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>−2</td>
</tr>
<tr>
<td>Construction of water distribution network</td>
<td>2</td>
<td>−1(1)</td>
<td>−2(1)</td>
<td>0</td>
<td>−1(2)</td>
<td>−1(1)</td>
<td>−2(1)</td>
<td>1(3)</td>
<td>1(2)</td>
<td>−1(1)</td>
<td>−4</td>
</tr>
<tr>
<td>Construction of storm water and industrial sewer</td>
<td>3</td>
<td>−1(1)</td>
<td>−1(1)</td>
<td>2(3)</td>
<td>−1(2)</td>
<td>−1(1)</td>
<td>−2(1)</td>
<td>1(3)</td>
<td>1(2)</td>
<td>0</td>
<td>−1(1)</td>
</tr>
<tr>
<td>Construction of industrial wastewater treatment plant</td>
<td>4</td>
<td>−1(3)</td>
<td>0</td>
<td>0</td>
<td>−1(2)</td>
<td>−1(1)</td>
<td>−2(1)</td>
<td>1(3)</td>
<td>1(2)</td>
<td>0</td>
<td>−1(1)</td>
</tr>
<tr>
<td>Transportation of workers</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1(5)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Construction of industrial units</td>
<td>6</td>
<td>−1(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1(5)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Industrial Solid waste disposal</td>
<td>7</td>
<td>−2(2)</td>
<td>−3(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>−1(1)</td>
</tr>
<tr>
<td>Required water (Industrial use)</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>−1(1)</td>
<td>−6</td>
</tr>
<tr>
<td>Operation of wastewater treatment plant</td>
<td>9</td>
<td>1(1)</td>
<td>−1(2)</td>
<td>0</td>
<td>−2(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>−1(1)</td>
<td>0</td>
<td>2(3)</td>
</tr>
<tr>
<td>Discharge of Industrial effluent</td>
<td>10</td>
<td>−2(1)</td>
<td>−3(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Industrial units operation</td>
<td>11</td>
<td>−2(3)</td>
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<td>0</td>
<td>−3(1)</td>
<td>−2(1)</td>
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<td>5(5)</td>
<td>5(5)</td>
<td>4(5)</td>
<td>−2(1)</td>
</tr>
<tr>
<td>Total action impact</td>
<td>12</td>
<td>−21</td>
<td>−23</td>
<td>−13</td>
<td>−7</td>
<td>−3</td>
<td>45</td>
<td>32</td>
<td>20</td>
<td>−1</td>
<td>37</td>
</tr>
</tbody>
</table>

A negative sign (−) in the front of the magnitude number shows that the impact is adverse (Table 2).
3.3.1. Quantitative Analysis. Excavation and embankment, construction of industrial units, water distribution network, and industrial wastewater collection system have a low magnitude effect with score of −2 (Table 7) and very low importance impact with score of 1 (Table 4) was considered. Therefore, as shown in Table 1, cell (6, 6), the net score for impact of “Construction of industrial units” on “Plant species” of the project area is equal to −2 [1 × (−2) = −2].

3.4. EIA of the Wildlife Zones. Environmental protected areas are not affected by the air and soil pollutants because of their distance from industrial estate. According to the location of the wildlife protected areas (southwest of the estate) and region wind rose (Figure 2), the percentage of wind to the southwest about 6 percent of the winds, blow into this region during the year. Therefore, these regions were not highly affected by pollutants. The pattern of prevailing winds in this estate indicated that these winds have west-east direction. Figure 4 shows the magnitude of air pollution effects on wildlife-protected areas.

3.5. EIA for Groundwater Quality via Matrix

3.5.1. Quantitative Analysis. As indicated in Table 1, cell (2, 10), importance effect of discharge of industrial effluents on ground water considered “low” with the score of 2, and medium and intermittent magnitude of effect considered with the score of −3 (Table 3).

Water resources of study area are provided by wells and Qanats, and there is no surface water resource in this area.
Table 3: Groundwater pollution potential by the industrial wastes.

<table>
<thead>
<tr>
<th>Pollution level</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous</td>
<td>Leakage of sewers and industrial wastewater treatment units</td>
<td>Leachate percolated from Industrial wastes landfills</td>
<td>Leakage of Industrial reactors, underground and aboveground reservoirs</td>
</tr>
<tr>
<td>Intermittent</td>
<td>Leakage of Industrial sites</td>
<td>Discharge of Industrial effluents</td>
<td>Suddenly and severe spills</td>
</tr>
<tr>
<td>Accidental</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Scope for importance of the effect for all of the impacts of the project.

<table>
<thead>
<tr>
<th>Importance of effect</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>No effect</td>
<td>0</td>
</tr>
<tr>
<td>Very low effect</td>
<td>1</td>
</tr>
<tr>
<td>Low effect</td>
<td>2</td>
</tr>
<tr>
<td>Important effect</td>
<td>3</td>
</tr>
<tr>
<td>Very important effect</td>
<td>4</td>
</tr>
<tr>
<td>Extremely important effect</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5: Ranking of magnitude effect on atmospheric stability classes.

<table>
<thead>
<tr>
<th>Effect magnitude</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class A: extremely unstable</td>
<td>1</td>
</tr>
<tr>
<td>Class B: unstable</td>
<td>2</td>
</tr>
<tr>
<td>Class C: slightly unstable</td>
<td>3</td>
</tr>
<tr>
<td>Class D: neutral</td>
<td>4</td>
</tr>
<tr>
<td>Class E: slightly stable</td>
<td>5</td>
</tr>
<tr>
<td>Class F: stable to extremely stable</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 6: Classification of pastures’ status.

<table>
<thead>
<tr>
<th>Status</th>
<th>Vegetation composition percentage in climax stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent (E)</td>
<td>81–100</td>
</tr>
<tr>
<td>Good (G)</td>
<td>61–80</td>
</tr>
<tr>
<td>Fair (F)</td>
<td>41–60</td>
</tr>
<tr>
<td>Poor (P)</td>
<td>21–40</td>
</tr>
<tr>
<td>Very poor (VP)</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

4. Discussion

This study found that more attention should be paid to the regions located in the zones with very high, high, and medium vulnerability than to other regions. These regions consisted of Koohpayeh city; the Qanats located in south and southwest of the industrial estate; gardens located in suburbs; the residential places that are located in the east of the industrial estate.

According to the transition of industrial estate pollutants, residential places located in the radius of 2500 meters of the city will be affected more. Koohpayeh city, which is the most populated center in this region, is more vulnerable because of its location, thus it needs more attention than other regions.

Regarding the natural environment aspects of conducting the project, the largest percentage of land use is related to the low-density pastures and the lowest percentage is devoted to residential areas.

The impact assessment is a management tool for stakeholders and decision makers; it serves as a supplementary tool for other engineering studies and economic projects.

Industrial ecosystem is an important approach for sustainable development. In an industrial environment, a group of industries are interconnected through mass and energy exchanges for mutual benefits. However, some mass and energy exchange activities may have unexpected environmental impact [10].

Industrial development could be defined as providing the foundation for industrial expansion and social stability with reducing the environmental destructive impacts. The necessity to achieve mentioned goal is to merge environmental concerns with different levels of policy making and controlling levels [8].

To predict, identify, and determine accurate analysis of positive and negative effects of an environmental project on
natural and man-made environments, it is necessary to evaluate these projects before their implementation to estimate the minimum negative consequences in the future. Thus, spatial analyzing tool can be used under water analyzing tool and destruction model in GIS.

The purpose of using these tools is preventing degradation and reduction of vulnerability level of ecosystems as well as prevention of the destruction in development programs. Moreover, some preventive ways against the short-term recurrence of destruction can be suggested. Therefore, it is vital to evaluate the environmental impacts of the industrial development to provide a clear management for the decision-makers and stakeholders. Environmental protection issues are considered as parts of the national laws, and application of such projects may be of help in this regard.

The main limitation of this study is its cross-sectional nature. Some damages caused by this development project such as groundwater contamination may have nonmeasurable environmental impact, which is not compensable.

5. Conclusion

Results of quantitative analysis of the effects of environmental factors on the industrial estate development project by the matrix method demonstrated that the sum scores allocated to the project activities on environmental factor is “+37,” which means that positive effects of project activities outweigh the drawbacks and totally it does not have detrimental effects on the environment and residential neighborhood (Table 8).

Given that the qualitative and quantitative analysis, industrial estate development project might have some negative effects on some environmental factors but generally, development of this estate should not be prevented. Moreover, with considering all factors including socio-economic factors that have special effect on development process, performing of the project with minimum negative consequences should be provided.

Acknowledgment

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References


Research Article

Ethylbenzene Removal by Carbon Nanotubes from Aqueous Solution

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The removal of ethylbenzene (E) from aqueous solution by multiwalled, single-walled, and hybrid carbon nanotubes (MWCNTs, SWCNTs, and HCNTs) was evaluated for a nanomaterial dose of 1 g/L, concentration of 10–100 mg/L, and pH 7. The equilibrium amount removed by SWCNTs (E: 9.98 mg/g) was higher than by MWCNTs and HCNTs. Ethylbenzene has a higher adsorption tendency on CNTs, so that more than 98% of it adsorbed in first 14 min, which is related to the low water solubility and the high molecular weight. The SWCNTs performed better for ethylbenzene sorption than the HCNTs and MWCNTs. Isotherms study indicates that the BET isotherm expression provides the best fit for ethylbenzene sorption by SWCNTs. Carbon nanotubes, specially SWCNTs, are efficient and rapid adsorbents for ethylbenzene which possess good potential applications to maintain high-quality water. Therefore, it could be used for cleaning up environmental pollution to prevent ethylbenzene borne diseases.

1. Introduction

Ethylbenzene (aromatic organic compound) is important on material in the chemical process industries. This material is usually used as raw material in numerous chemical productions and also often as solvent in a wide variety of manufacturing processes [1].

Ethylbenzene is widely used in industry as solvents for organic synthesis, equipment cleaning, and other down-stream processing purposes. They are present in refinery and chemical industry effluents. The ethylbenzene is frequently found in groundwater because of leaks in underground storage tanks and pipelines, improper waste disposal practices, inadvertent spills, and leaching from landfills [2]. This pollutant has been found to cause many serious health side effects to humans (e.g., skin and sensory irritation, central nervous system depression, respiratory problems, leukemia, cancer, and disturbance of the kidney, liver, and blood systems) [3].

Ethylbenzene removal from groundwater has been widely studied, and several processes have been successfully applied. A considerable effort has been dedicated in the past years concerning the removal of ethylbenzene from water and wastewater, several methods have been proposed and developed, and the most extensively used is adsorption process.

Carbon nanotubes (CNTs) have attracted great interest because of their unique chemical structure and intriguing physical properties [4]. The large adsorption capacity of CNTs for organic pollutant is primarily due to their pores structure and the existence of a wide spectrum of surface functional groups. The adsorption mechanism of ethylbenzene on CNTs is mainly attributed to the π-π electron donor-acceptor interaction between the aromatic ring of ethylbenzene and the surface carboxylic groups of CNTs [5].

The adsorption of ethylbenzene on Pt and on epitaxial FeO and Fe3O4 films is studied by Ranke and Weiss [6]. Lu et al. used surface modification of carbon nanotubes to enhance ethylbenzene adsorption from aqueous solutions. The NaOCl-oxidized CNTs have superior adsorption performance toward ethylbenzene with many types of carbon and silica adsorbents reported in the literature [5]. Su et al. employed multiwalled carbon nanotubes (MWCNTs) that
were oxidized by sodium hypochlorite (NaOCl) solution to enhance the adsorption of ethylbenzene in an aqueous solution [7]. Aivalioti et al. studied the removal of ethylbenzene from aqueous solutions by raw (DR) and thermally modified diatomite [3].

These studies indicate that CNTs have high affinity with both organic and inorganic chemicals. Literature also showed the potential for developing carbon nanotube technologies for treating ethylbenzene in water. It is commonly discharged from many kinds of industrial activities and frequently encountered in the groundwater of gasoline-contaminated sites [3–7].

The present study aimed to determine the removal efficiency for ethylbenzene using single-walled and multi-walled carbon nanotubes and hybrid carbon nanotubes and to rank their ethylbenzene removal abilities. The contribution of this study is the evaluation of using hybrid CNTs in ethylbenzene removal that was not found in the literature.

2. Materials and Methods

2.1. Materials. The chemical tested in this study was ethylbenzene (Merck, purity: 99.7%). A stock solution of approximately 100 mg/L of ethylbenzene was prepared by dissolving appropriate amounts of substance in a standard solution that contained 100 mg/L of ethylbenzene in deionized H2O. The mixture was mixed thoroughly by using an ultrasonic bath (BANDELIN Sonorex Digtec) for 60 min. Then, it was stirred continuously for 24 h at 25°C. After shaking, the solution was put in the ultrasonic bath again for 30 min and was used to prepare the initial ethylbenzene solution with a 10–100 mg/L concentration. Finally, standard series and samples were prepared using deionized H2O to achieve the desired concentrations.

2.2. Experimental Conditions. Batch adsorption experiments were conducted using 110 mL glass bottles with the addition of 100 mg of adsorbents and 100 mL of ethylbenzene solution at an initial concentration (C0) of 10 mg/L. It was chosen to be representative of low ethylbenzene level in water polluted with gasoline. The glass bottles were sealed with 20 mm stoppers. The headspace within each beaker was minimized to exclude any contaminant volatilization phenomena. The glass bottles from the batch experiments were placed on a shaker (Orbital Shaker Model OS625) and were stirred at 240 rpm at room temperature for 10 minutes. The solution samples were then allowed to settle for 2 min. Finally, the ethylbenzene concentration in the liquid phase was determined using gas chromatography with detector of mass spectrometry (GC/MS). All of the experiments were repeated three times, and only the mean values were reported. Blank experiments, without the addition of adsorbents, were also conducted to ensure that the decrease in ethylbenzene concentration was not due to adsorption on the wall of the glass bottle or volatilization. The pH was adjusted to neutral using 0.05 M HCl or 0.05 M NaOH. The amount of adsorbed ethylbenzene on the adsorbents (qe, mg/g) were calculated as follows:

\[ q_e = \frac{(C_0 - C_t) \times V}{m}, \]  

where \( C_0 \) and \( C_t \) (mg/L) are the ethylbenzene concentrations at the beginning and after a certain period of time, \( V \) is the initial solution volume (L), and \( m \) is the adsorbent weight (g).

2.3. Chemical Analysis. An Agilent Technologies system consisting of a 5975C inert MSD with a triple-axis detector equipped with a 7890A gas chromatograph with a split/splitless injector was used for ethylbenzene measurements. A fused silica column, HP-5 ms (5% phenyl-95% dimethylpolysiloxane; 30 m × 0.25 mm I.D., 0.25 μm), was employed with helium (purity 99.995%) as the carrier gas at a flow rate of 1 mL/min. The column temperature was programmed as follows: 36°C for 2 min, increasing to 140°C at 10°C/min and holding for 6 min. The injector port was maintained at 210°C, and a 1 mL volume of headspace was injected in splitless mode (2.0 min). The effluent from the GC column was transferred via a transfer line held at 280°C and fed into a 70 eV electron impact ionization source held at 280°C. The data were acquired and processed by the data analysis software.

Static headspace analysis was performed using a CTC PAL-Combi PAL headspace sampler. The experimental parameters of the headspace sampler were as follows: incubation time, 25 min; incubation temperature, 70°C; sample loop volume, 1 mL; syringe/transfer line temperature, 110°C; flush time, 2 min with N2; loop fill time, 0.03 min; injection time, 1 min; and sample volume, 10 mL in 20 mL vials. No NaCl was added to the samples.

The pH measurements were made with a pH meter (EUTECH, 1500).

2.4. Adsorbents. During the experimental procedure, three different nanomaterials were tested: (1) single-walled carbon nanotubes (SWCNTs), (2) multi-wall carbon nanotubes (MWCNTs), and (3) hybrid carbon nanotubes (HCNTs). The SWCNTs with 1-2 nm diameter (Figure 1), MWCNTs with 10 nm diameter (Figure 2), and HCNTs were a hybrid of MWCNTs and silica (Figure 3) to open the tubes of MWCNT as a sheet instead of tube. These adsorbents were purchased from the Iranian Research Institute of the Petroleum Industry.

2.5. Analysis of Data. For the data analysis, design of experiments (DOE) software (Design Expert 6) was used. In this software, the analysis was done with a general factorial plan. Isotherm Fitting Tool (ISOFIT) is a software program that fits isotherm parameters to experimental data via the minimization of a weighted sum of squared error (WSSE) objective function. ISOFIT supports a number of isotherms, including (1) Brunauer-Emmett-Teller (BET), (2) Freundlich, (3) Freundlich with Linear Partitioning (F-P), (4) Generalized Langmuir-Freundlich (GLF), (5) Langmuir, (6) Langmuir with Linear Partitioning (L-P), (7) Linear, (8) Polanyi, (9) Polanyi with Linear Partitioning (P-P), and (10) Toth. Observation weights are ideally assigned according to individual estimates of measurement error, such that \( w_i = 1/sd_i \), where \( sd_i \) is the standard deviation of the ith measurement.
2.6. Recycling Method. The reversibility of the sorbents that were used for ethylbenzene removal from aqueous solution was evaluated via 2 successive adsorption cycles followed by 2 successive desorption cycles. Recycling was also conducted at 105 ± 2°C and 24 h in an oven (Memmert D-91126, Schwabach FRG). All samples were replicated at least in triplicate.

3. Results and Discussion

3.1. Adsorption Performance. Table 1 shows the ethylbenzene removal percent for MWCNTs, SWCNTs, and HCNTs under an initial ethylbenzene concentration of 10 mg/L, an adsorbent concentration of nanomaterial of 1000 mg/L, contact time of 10 min, and shaking at 240 rpm.
Table 1: Ethylbenzene removal by MWCNT, SWCNT, and HCNT at $C_0 = 10$ mg/L and contact time of 10 min.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>$C_t$ (mg/L)</th>
<th>Removal percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>0.23</td>
<td>91.7</td>
</tr>
<tr>
<td>SWCNT</td>
<td>0.03</td>
<td>99.5</td>
</tr>
<tr>
<td>HCNT</td>
<td>0.04</td>
<td>97.6</td>
</tr>
</tbody>
</table>

Based on the DOE analysis, there were differences between MWCNTs, SWCNTs, and HCNTs for ethylbenzene removal (values of “Prob > |t|” less than 0.05).

Figure 4 shows the ethylbenzene removal by MWCNTs, SWCNTs, and HCNTs and a comparison between them. SWCNTs were better than HCNTs and MWCNTs, and also HCNTs were better than MWCNTs at removing ethylbenzene.

Table 2: Ethylbenzene removal by raw and recycled MWCNTs, SWCNTs, and HCNTs at $C_0 = 10$ mg/L and contact time of 10 min.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$C_t$ (mg/L)</th>
<th>Removal percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTrec1</td>
<td>1.16</td>
<td>88.5</td>
</tr>
<tr>
<td>SWCNTrec1</td>
<td>0.01</td>
<td>99.8</td>
</tr>
<tr>
<td>HCNTrec1</td>
<td>0.35</td>
<td>96.5</td>
</tr>
<tr>
<td>MWCNTrec2</td>
<td>1.37</td>
<td>86.3</td>
</tr>
<tr>
<td>SWCNTrec2</td>
<td>0.23</td>
<td>97.7</td>
</tr>
<tr>
<td>HCNTrec2</td>
<td>0.43</td>
<td>95.7</td>
</tr>
</tbody>
</table>

Figure 5 indicates the equilibrium amounts of ethylbenzene adsorbed on MWCNTs, SWCNTs, and HCNTs ($q_e$) with a $C_0$ of 10 mg/L and contact time of 10 min.

The results from this study showed that the $q_e$ for SWCNTs is higher than for HCNTs and MWCNTs. With
Table 3: Summary of selected diagnostics for ethylbenzene adsorbed by CNTs.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Selected diagnostics</th>
<th>Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GLF</td>
<td>Toth</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>AICc 34.4</td>
<td>0.962</td>
</tr>
<tr>
<td></td>
<td>$R^2_1$ 0.988</td>
<td>0.962</td>
</tr>
<tr>
<td></td>
<td>$R^2_2$ 0.934</td>
<td>0.892</td>
</tr>
<tr>
<td></td>
<td>$M^2$ 30</td>
<td>1 $\times$ 10$^{-9}$</td>
</tr>
<tr>
<td></td>
<td>Linear</td>
<td>Non-linear</td>
</tr>
</tbody>
</table>

| HCNTs      | AICc 25.9            | 26.3      | 26.3 26.3        | 26.3 | 29.5 | 29.5       | 31.3 | 40.7 | 72.8   |
|            | $R^2_1$ 0.994        | 0.992     | 0.992 0.992      | 0.992 | 0.992 | 0.992 0.992 | 0.992 | 0.960 | 0.000 |
|            | $R^2_2$ 0.946        | 0.942     | 0.942 0.942 0.942 | 0.942 | 0.942 | 0.942 0.942 | 0.952 | 0.945 | 0.957 |
|            | $M^2$ 83             | 6 $\times$ 10$^{-10}$ | 1 $\times$ 10$^{-9}$ | 8 $\times$ 10$^{-10}$ | 6 $\times$ 10$^{-10}$ | 3 $\times$ 10$^{2}$ | 20 | 5 $\times$ 10$^{-1}$ | 10 | 2 $\times$ 10$^{8}$ |
|            | Linear               | Non-linear | Linear | Linear Non-linear | Non-linear | Linear Non-linear | Linear Non-linear | Linear |

| MWCNTs     | AICc 30.7            | 34.8      | 34.8 34.8 34.8 | 34.8 | 34.8 | 38.6       | 39.3 | 37.6 | 68.1   |
|            | $R^2_1$ 0.989        | 0.980     | 0.980 0.980 0.980 | 0.980 | 0.980 | 0.979 0.980 | 0.979 | 0.965 | —      |
|            | $R^2_2$ 0.931        | 0.914     | 0.914 0.914 0.914 | 0.914 | 0.914 | 0.914 0.914 | 0.918 | 0.956 | 0.944 |
|            | $M^2$ 39             | 1 $\times$ 10$^{-9}$ | 2 $\times$ 10$^{-9}$ | 2 $\times$ 10$^{-9}$ | 2 $\times$ 10$^{-9}$ | 2 $\times$ 10$^{-9}$ | 11 | 5 $\times$ 10$^{-1}$ | 11 | 3 $\times$ 10$^{-9}$ |
|            | Linear               | Linear    | Linear | Linear Non-linear | Non-linear | Linear Non-linear | Linear Non-linear | Linear |

AICc: Multimodel ranking, $R^2_1$: Correlation between measured and simulated observation, $R^2_2$: Correlation between residual and normality, $M^2$: Linssen measure of nonlinearity.

A $C_0$ of 10 mg/L, the SWCNTs showed the greatest $q_e$ (ethylbenzene: 9.98 mg/g). The equilibrium amount ($q_e$) for ethylbenzene adsorption sequence is SWCNTs > HCNTs > MWCNTs.

Equilibrium amount from Lu et al. study for surface modification of carbon nanotubes $q_e$ for ethylbenzene obtained 180 mg/g for a $C_0$ of 60 mg/L [5]. And in study of Aivalioti et al., $q_e$ for ethylbenzene adsorbed by raw diatomite soil and thermally modified diatomite were 0.3 and 0.6 mg/g, respectively [3]. The equilibrium results from Su et al. study showed that the $q_e$ of ethylbenzene adsorption (at a $C_0$ of 200 mg/L, contact time of 240 min, and 600 mg/L of adsorbent concentration) by raw CNT and modified CNT by NaOCl were 255 and 274 mg/g, respectively [7].

The results imply the presence of chemically inherited groups that lead to direction of the affinity for ethylbenzene removal, irrespective of the texture characteristics. This indicates that the adsorption of ethylbenzene on CNTs is dependent on the surface chemical nature and the porosity characteristics. Similar findings have been reported in the literature for the adsorption of ethylbenzene on activated carbon [8] and multiwalled carbon nanotubes (MWCNTs) [5, 7].

As shown in Figure 3 used of silica with MWCNT as HCNT, silica cause opens the tubes of MWCNTs and produce sheet of carbon nanotubes, which have more area than MWCNTs for ethylbenzene adsorption. It is response for more removal of ethylbenzene by HCNTs than MWCNTs.

Furthermore, the electrostatic interaction between the ethylbenzene molecules and the SWCNT surface may also explain the observation of high ethylbenzene adsorption via the single-walled CNTs. Because the ethylbenzene molecules are positively charged [5], the adsorption of ethylbenzene is thus favored for adsorbents with a negative surface charge. This results in more electrostatic attraction and thus leads to a higher ethylbenzene adsorption.

Under analogous conditions, the present SWCNTs and HCNTs show better performance for ethylbenzene adsorption than do other adsorbents. This suggests that the SWCNTs and HCNTs are efficient ethylbenzene adsorbents. Because the costs of commercially available HCNTs are continuously decreasing, it may be possible to utilize these novel nanomaterials for ethylbenzene removal in water and wastewater treatment in the near future.

3.2. CNTs Recycling. Repeated availability is an important factor for an advanced adsorbent. Such adsorbent not only possesses higher adsorption capability, but also should show better desorption property, which will significantly reduce the overall cost for the adsorbent.

Although CNTs show more ethylbenzene sorption capacities form aqueous solution, very high unit cost currently restricts their potential use in water and wastewater treatment. Thus, testing the reversibility of sorbents used for ethylbenzene removal is required in order to reduce their replacement cost. For this purpose as a part of the study, probability for used SWCNTs, MWCNTs, and HCNTs recycling was investigated. Table 2 shows the ethylbenzene removal percent by MWCNTs, SWCNTs, and HCNTs that were recycled in the first cycle (MWCNTrec1, SWCNTrec1, and HCNTrec1) and MWCNTs, SWCNTs, and HCNTs that were recycled in the second cycle (MWCNTrec2, SWCNTrec2, and HCNTrec2) under initial ethylbenzene concentration of 10 mg/L, nanomaterial concentration of 0 mg/L, contact time of 240 min, and 600 mg/L of adsorbent concentration.
1000 mg/L, contact time of 10 min, and shaking at 240 rpm. Figure 6 compares raw SWCNTs, HCNTs, and MWCNTs with their recycling in cycles of 1 and 2.

It is apparent that CNTs can be reused for the removal of ethylbenzene through a large number of water and wastewater treatment and regeneration cycles. The presence of metal catalysts in raw SWCNTs that could be retained through the chemical process to functionalize of SWCNTs may be removed due to heating and cause better adsorption performance for recycled SWCNTs than raw SWCNTs. Also the structure and nature of carbon surface were changed after thermal treatment including the increase in graphitized structure and the decrease in surface functional groups and negative charges [9]. These specifications of SWCNTs cause more adsorption of ethylbenzene.

Results show that the ethylbenzene adsorbed by the SWCNTs, MWCNTs, and HCNTs could be easily desorbed by temperature, and thereby they can be employed repeatedly in water and wastewater management. This is the key factor for whether a novel but expensive sorbent can be accepted by the field or not. It is expected that the unit cost of CNTs can be further reduced in the future by recycling heat processes. So; the SWCNTs, HCNTs, and MWCNTs appear possibly cost effective ethylbenzene sorbents in water and wastewater treatment.

As CNTs and carbonaceous materials such as black carbon, coal, and kerogen in soils/sediments that are composed of almost the same element, desorption difference may be due to their distinct geometric structure. The carbonaceous materials exhibit a high degree of porosity and extended interparticulate surface area, whereas CNTs are one dimensional hollow nanosize tubes as well as aggregates. CNTs easily adhere to each other and form bundles due to strong Van der Waals interactions. The adsorption sites are therefore defined for the entire bundles instead of individual nanotubes. There are four possible groups of adsorption sites on bundles, including interior of individual tubes, interstitial channels between nanotubes, external groove sites, and the outer surface sites of individual tubes on the peripheral surface of the bundles. The interior of individual tubes is only available in open-ended tubes; the interstitial channels are applied for large tube diameters, while grooves and the external surface are of most importance for adsorption [4]. Therefore, it is inferred that most of the ethylbenzene is located on the external adsorption sites. Moreover, CNTs cannot form closed interstitial spaces in their aggregates. Hence, ethylbenzene adsorbed release due to temperature.

The sorbent weight loss was neglected in the recycling processes. The weight loss can be attributed to the evaporation of adsorbed water and the elimination of carboxylic groups and hydroxyl groups on the CNT wall [5].

3.3. Isotherm Study. The adsorption equilibrium data of ethylbenzene on SWCNTs, HCNTs, and MWCNTs samples were fitted by several well-known isotherm models to assess their efficacies. In this study, ISOFIT was applied to involving the adsorption of ethylbenzene with initial concentration of 10–100 mg/L (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L) by SWCNTs, HCNTs, and MWCNTs. Water solubility ($S_w$) of ethylbenzene was estimated 152 mg/L at pH 7. Numerous studies have considered one or more of the supported isotherms in the context of a water-wastewater system. The dual-mode isotherms reflect recently developed models for the sorption of hydrophobic organic solutes [10].

To characterize parameter uncertainty, ISOFIT reports parameter correlation coefficients and 95% linear confidence intervals for each isotherm parameter. The correlation coefficient (CORij) between parameters Xi and Xj is a measure of the linear dependence between the two parameters; values range from −1 to 1, with a value of zero (0) indicating no correlation.

Isotherm expressions are important for describing the partitioning of contaminants in environmental systems. Table 3 summarizes some of the diagnostic statistics computed by ISOFIT and reported in the output file for ethylbenzene adsorption by CNTs.

Figure 7 contains plots of the fitted isotherms for ethylbenzene adsorption by SWCNTs: (a) Toth, P-P, GLF, and Polanyi, (b) linear, Freundlich, Langmuir, F-P and L-P isotherm, and (b) BET isotherm.

![Figure 7: Plots of fitted isotherms and observed data of ethylbenzene adsorption by SWCNTs: (a) Toth, P-P, GLF, and Polanyi, (b) linear, Freundlich, Langmuir, F-P, L-P, and BET.](image)
Figure 8: Plots of fitted isotherms and observed data of ethylbenzene adsorption by HCNTs: (a) Toth, P-P, GLF, and Polanyi, (b) linear, Freundlich, Langmuir, F-P, L-P, and BET.

Figure 9: Plots of fitted isotherms and observed data of ethylbenzene adsorption by MWCNTs: (a) Toth, P-P, GLF, and Polanyi, (b) linear, Freundlich, Langmuir, F-P, L-P, and BET.

Wibowo et al. studied the adsorption of benzene and toluene from aqueous solutions onto activated carbon; their study shows that the Langmuir equation can describe the experimental data fairly well than Freundlich [1].

In the adsorption mechanism of aromatic compounds in liquid phase on SWCNT, there are two main types of interactions, including electrostatic and dispersive. The functional group linked to the adsorptive aromatic ring can activate or deactivate it that removes its electronic charge. Electron with drawing groups on an aromatic ring create a partial positive charge in the ring, while deactivating groups produce the opposite effect, creating a partial negative charge [1].

Here, ethylbenzene is in the molecular form in the aqueous solution; in this case, dispersive interactions are predominant, mainly because of the attraction between the π orbital on the SWCNT basal planes and the electronic density in the benzene and toluene aromatic rings (π-π interactions) [1].

The limitations of this study were using constant condition for ethylbenzene removal. Somewhat separation of nanotubes from supernatant was also difficult. Carbon nanotubes are in the nano of one dimension. Also, to
provide a well adsorption; ethylbenzene should penetrate into the tubes. This causes slow absorption, and increasing the contact time is required. Similar findings have been reported in the literature for the adsorption of ethylbenzene by multiwalled carbon nanotubes (MWCNTs) [7]. But, in the hybrid nanotubes sheets, these tubes are opened and contact surfaces are more easily available.

4. Conclusion

We concluded that SWCNTs showed a higher adsorption capacity for ethylbenzene removal than MWCNTs and HCNTs. Also between MWCNT and HCNT, HCNT shows better performance for ethylbenzene removal because of sheet shape produced by silica. It appears that ethylbenzene is the component with higher adsorption tendency on CNTs. The equilibrium amount \( q_e \) sequence is SWCNTs > HCNTs > MWCNTs.

Results of CNTs recycling show that the ethylbenzene adsorbed by the SWCNTs, MWCNTs, and HCNTs could be easily desorbed by temperature, and thereby they can be employed repeatedly in water and wastewater management.

ISOFIT provided superior fits for the BET isotherm for ethylbenzene removal by SWCNTs, and GLF fits for ethylbenzene removal by HCNTs and MWCNTs.

More research works on the toxicity of CNTs and CNT-related materials are needed before practical use of CNTs in water and wastewater treatment because it can be realized.

Acknowledgment

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References


Research Article

Community-Led Assessment of Risk from Exposure to Mercury by Native Amerindian Wayana in Southeast Suriname

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This study was a collaboration between Western public health researchers and Suriname indigenous communities. The question asked was “how can Western researchers effectively engage traditional indigenous communities in Suriname, South America, in public health research”. The approach used a combination of Participatory Action Research methods in which “Western” researchers became participating observers in an indigenous-led research initiative. The Wayana communities of Puleowime (Apetina) and Kawemhakan (Anapayke) defined a single objective: determine for themselves whether they are at risk from exposure to mercury (Hg) contamination. Community members collected hair samples for analysis. Hair samples were analyzed using a portable Hg analyzer. Individual, community and hazard quotient indices were used to quantify risk. Results showed the Wayana were at a high lifetime risk of adverse effects from exposure to Hg. This study showed that the community-led approach is an effective way Westerners can engage indigenous communities and address serious public health threats. While factors that appealed to indigenous communities were identified, obstacles inherent to Western research methodology were also encountered.

1. Introduction

This study began in 2007 with one overarching objective, which was for Wayana communities in southeast Suriname to determine for themselves the risk of exposure to contaminants from mining, especially mercury (Hg), on their health. To this end, a community-led research design was created in partnership between community leaders in two Wayana villages and two non-governmental organizations. Community leaders represented the perspective and interests of community members and as such defined the context, the research problem and led the exploration of culturally appropriate public health solutions. Community leaders invited two non-governmental organizations to assist them in designing and carrying out an environmental risk assessment study. The Suriname organization Stichting Wadeken Wasjibon Maria (SWWM) provided guides, educators, and translators, whereas the USA-based Suriname Indigenous Health Fund (SIHF) provided expertise by a toxicologist, a sociologist, and a public health physician.

Indigenous villages in Suriname's interior region are dependent on their traditional lands for hunting, fishing, farming, medicines, shelter, and their daily necessities such as clean water [1]. Many of these people have been displaced from their lands due to mining concessions [2]. Kawemhakan is an example. Families are relocating from the Suriname side of the Lawa River to the French Guiana side because of pollution of their traditional water source by gold mining activities. Gold mining activities release mercury (Hg) into the water. Methylation of inorganic Hg released by mining leads to fish contamination, and fish are the primary source of protein for these communities. Hg toxicity causes irreversible damage to the environment and to the health of the general population living in the region where mining occurs.

Since the end of the last century, gold mining in Suriname has been carried out at numerous sites and still continues to be practiced by international mining companies and smaller groups on terrestrial sites or by dredging operations directly in the rivers. In Suriname it is estimated
that 20,000 kg/year Hg is discarded into the environment by small-scale and artisanal gold mining [3, 4]. Other studies estimate that gold mining releases 9,000–54,000 kgs of Hg in Suriname interior rainforest [5]. This amount is orders of magnitude larger than other sources including Hg from bauxite refining and biomass [6]. Emissions by bauxite refining were estimated to be 500–600 kg/year in 2002-2003 and below 150 kg/year in 2005 from the “Suriname Aluminum Company.” Emissions from biomass burning are estimated to be about 30 kg/year.

A range of health outcomes is expected when communities like the Wayana live close to resources valuable to mainstream society. Resource exploitation often affects indigenous people negatively either through exposure to environmental contamination or by restricting their access to forest areas that provide living space, medicinal organisms, food, building materials, and water [7]. The maintenance of traditional culture is thought to be a protective factor, especially for problems related to nutrition.

Gold mining activities are mainly concentrated within an area of Eastern and Southeastern Suriname (Figure 1). This region is rich in minerals, including gold. And at the same time, it is rich in biodiversity and is inhabited by a variety of indigenous (Amerindian) and tribal (Maroon) communities. The significance of this study, conducted by the communities Puleowime (Apetina) and Kawemhakan (Anapayke), is not limited to the Greenstone Belt Region (GBR) because the direct impacts of mining go well beyond the geological boundaries of the GBR [8]. The impacts of gold mining in Suriname fall into four general categories: physical, chemical, biological, and social. Specific examples of impacts include the degradation of landscapes and soils, altered hydrogeological regimes, modification of surface drainage, degradation of drinking water resources, degradation of surface water by increased turbidity, contamination of land and water by solid and liquid waste and mercury, loss of natural habitats and biodiversity, loss of rare and endangered species, degradation of fisheries, and finally the degradation of the social integrity and physical health of indigenous communities living in the region where gold mining occurs. The villages of Puleowime (Apetina) and Kawemhakan (Anapayke) are home to the Wayana Tribe, a collective name for several ethnic groups including the Upului, Opagwana, and Kukuiyana [9, 10].

Mercury contamination is of particular importance to indigenous communities in the region. In neighboring French Guiana, a mercury risk assessment study was conducted in 1994, where hair samples were analyzed for Hg [11]. Results showed high levels of Hg, only in the native Amerindian communities living in the upper reaches of the Maroni River. This contamination probably reflects past and current gold mining activities in this area and is linked to the diet of these populations, of which fish is a main component. This population’s health is a major concern for France because the Wayana is an ethnic group that may be vulnerable due to their particular way of life.

In Suriname, numerous risk assessment studies reporting the effects of Hg pollution on public health have been performed. However, few studies have been published. Recent studies have shown high levels of Hg in people from interior communities on the Saramacca River [12]. Hg vapor from gold shops in the capital also contributes to exposure of people in their vicinity even if it is difficult to assess [13]. Communities are aware of their exposure to Hg, its link to gold mining, and the potential for neurological toxicity. However, the majority of individuals remain poorly informed about the precise causes, symptoms, and possible remedies [12].

Suppression of public health research on the impacts of mining and Hg contamination from gold mining by government and non-government organizations is obscuring the public health risks and leading to insufficient and misguided regulation. [Americaanse Wetenschapper Gevlucht uit Suriname: Na bedreiging ATM: Americaanse wetenschapper gevlucht uit Suriname (American Scientist Escaped from Suriname after threat from ATM) De West Newspaper, Paramaribo, Suriname, 19 July 2005]. Foreign researchers and in-country collaborators were warned of “dire consequences” if they communicate the effects on public and environmental health from Hg contamination from gold mining. The defenders of scientific censorship claim that the government has the right to set policy and deliver its own message in its own words. Under this system, research is highly institutionalized through disciplines and fields of knowledge. Research is also an integral part of political structures: funding agencies, universities, development programs, and policies. Research is regarded as being the domain of experts who have advanced educational qualifications and have access to highly specialized language, skills and resources [14].

While it is reasonable to require that scientists defend data and clarify statements, it is essential that research conducted at the intersection of race and economic class avoid the biases caused by Western systems for organizing, classifying, and storing new information, and for theorizing the meanings of such discoveries [14]. Indigenous communities are now calling for an end to “the ambulance at the bottom of the cliff approach to health” and are calling for support for projects using culturally appropriate, community-directed prevention and intervention strategies [2, 14]. This form of research is a pragmatic integration of both scientific and traditional knowledge systems. Western science focuses on hypothesis testing by data collection and statistical analysis. Indigenous traditional knowledge is based on cumulative experience, close observation, and oral knowledge communicated by elders and handed down over generations. This study worked with Wayana community leadership to create a collaborative environmental health research project.

Wayana village leaders and participating villagers from Puleowime (Apetina) and Kawemhakan (Anapayke) in Surname SE Lawa region (Figure 1) consistently prioritized three concerns facing their communities: (1) encroachment of their traditional homeland by miners who are heavily armed and prevent villagers from hunting, fishing, and providing for their families; (2) the effects of water and food chain contaminants from mining, especially nervous system damage from mercury (Hg) on their health; (3) clean water for drinking, cooking, and bathing is now scarce
due to contamination from mining. (Testimony collected by authors during visit to Apetina 2008).

This study focused on item 2 and had one objective: Employ Participatory Action Research methods [15], participatory research methods [16], and the methods described by Smith [14] to conduct community-directed research so that two indigenous communities, Puleowime (Apetina) and Kawemhakan (Anapayke), with assistance from two charitable nonprofit organizations, could determine for themselves whether they were at risk from exposure to Hg contamination.

2. Methods and Materials

2.1. Community-Led Research. In 2008, community members in Puleowime (Apetina) pointed to the frequency with which they have been overstudied and note that research conducted by the World Wildlife Fund in 2004 was done with little concern for community needs. [Personal communication from Leon Eric Wijngaarde, Director of Stichting Wadeken Wasjibon Maria and Sita Tempico, board member from Kawemhakan (Anapayke), 2008. (Stichting Wadeken Wasjibon Maria is a self-organized nonprofit foundation comprised of native Amerindian representatives from various communities in Suriname)]. In 2008, Stichting Wadeken Wasjibon Maria (SWWM) acquired the data from the 2004 study then met with village leaders to discuss community rights in research, data ownership and to interpret study results in terms of the health impacts of contaminant exposure. SWWM, a public health and indigenous advocacy non-governmental organization in Suriname, was then invited to meet with representatives from Kawemhakan (Anapayke) to discuss community needs. Leaders from both communities concluded that they wanted to determine for themselves whether they were at risk from exposure to Hg contamination and assess potential health impacts from Hg exposure, especially in children. Because community leaders had previously been criticized for releasing data to the press, they determined they wanted findings to be published in an “international peer-reviewed journal” that would be acknowledged as legitimate by domestic and foreign government health care agencies. Stichting Wadeken Wasjibon Maria (SWWM) requested the assistance of the Suriname Indigenous Health Fund (SIHF), a nonprofit non-governmental organization based in the United States, to provide technical expertise throughout the research process. A toxicologist, a sociologist, and public health physician represented SIHF on the research team.

The approach used was a combination of Participatory Action Research methods [15], participatory research methods [16], and the methods described by Smith [14]. These approaches drew on a Freirean approach that is a collaborative and collegiate process [17]. The elements of the community-led research process are as follows: (1) outside science experts were issued an invitation by community members to participate in a codirected study; (2) community members codeveloped a research plan according to appropriate scientific procedures and traditional cultural norms; (3) data was collected by trained community members; (4) data was owned and interpreted by community members; (5) the final determination for the disposition of research results was determined by community members according to traditional decision-making processes.
2.2. Analysis of Hg Levels in Human Hair. Leaders from Puleowime (Apetina) and Kawemhakan (Anapayke) chose to collect hair samples for analysis (as opposed to blood or urine) because it is the least invasive sample to collect and the best indicator of dietary exposure to Hg from fish. Community members received training from SWWM educators and collected hair samples for analysis using methods designed to maximize sample quality and consistency and minimize cross-contamination, which emphasized the use of powderless surgical gloves and new, sterile, stainless steel scissors for each sample collected. Community members, with the assistance of representatives from the SWWM, collected and submitted hair samples for Hg analysis from 158 people in Puleowime (Apetina) and 106 people in Kawemhakan (Anapayke). Ages ranged from less than one-year to over 80 years old in both communities. In Puleowime, participants was more female (54 and 52, resp.) than male (67). In Kawemhakan, the number of males and females were almost the same (54 and 52, resp.). All hair samples were collected from the lower occipital region. When long hair strands (>3 cm) were collected, the hair tips were discarded and only the proximal 1 cm were used.

Each hair sample, of approximately 20 mg, was placed in a labeled envelope. The hair samples were analyzed in triplicate for total Hg by a SIHF technician educated in analytical chemistry and trained in the operation of the Lumex Hg analyzer. Hg analysis was by the cold-vapor technique using the Portable Zeeman Lumex (RA915*/RP-91C) mercury analyzer. The instrument detection level was 0.2 ng/g. All concentrations were expressed in parts per million (equal to µg/g Hg). Measurement of Hg levels in hair using the Lumex RA915*/RP-91C portable analyzer had been previously confirmed by laboratory analysis using a modified National Institute for Occupational Safety and Health (NIOSH) 6009 method. In this study, the Lumex was operated in software “On Stream” mode using the procedure in the manufacturer’s operation manual. NIST traceable standards 2709 for Hg at 1400 ng/g and 1633d for Hg at 91C) mercury analyzer. The instrument detection level was 0.2 ng/g. All concentrations were expressed in parts per million (equal to µg/g Hg). Measurement of Hg levels in hair using the Lumex RA915*/RP-91C portable analyzer had been previously confirmed by laboratory analysis using a modified National Institute for Occupational Safety and Health (NIOSH) 6009 method. In this study, the Lumex was operated in software “On Stream” mode using the procedure in the manufacturer’s operation manual. NIST traceable standards 2709 for Hg at 1400 ng/g and 1633d for Hg at 91C) mercury analyzer. The instrument detection level was 0.2 ng/g. All concentrations were expressed in parts per million (equal to µg/g Hg). Measurement of Hg levels in hair using the Lumex RA915*/RP-91C portable analyzer had been previously confirmed by laboratory analysis using a modified National Institute for Occupational Safety and Health (NIOSH) 6009 method. In this study, the Lumex was operated in software “On Stream” mode using the procedure in the manufacturer’s operation manual. NIST traceable standards 2709 for Hg at 1400 ng/g and 1633d for Hg at 91C) mercury analyzer. The instrument detection level was 0.2 ng/g. All concentrations were expressed in parts per million (equal to µg/g Hg). Measurement of Hg levels in hair using the Lumex RA915*/RP-91C portable analyzer had been previously confirmed by laboratory analysis using a modified National Institute for Occupational Safety and Health (NIOSH) 6009 method. In this study, the Lumex was operated in software “On Stream” mode using the procedure in the manufacturer’s operation manual. NIST traceable standards 2709 for Hg at 1400 µg/g, were used to standardize the analyzer before and after each ten samples analyzed.

SWWM and SIHF consulted with the communities throughout the process. Following the analysis of all hair samples, meetings were held to discuss the results and answer any questions the community had regarding the data. Afterwards, a community meeting was held to reflect on the process, outcome, and future needs. A physician was in attendance to answer questions from the community. The attending physician performed limited examinations on persons who requested a consultation because they thought they had been exposed to potentially hazardous levels of mercury. The purpose of this examination was to address their concerns, alleviate anxiety, determine whether their concerns had merit, and provide a baseline for future health monitoring. The examination by the physician included a discussion regarding the patients medical history, with emphasis on the nervous system (target organ for chronic exposure), the kidneys (target organ for acute and chronic exposure), the oral cavity (target organ for chronic exposure), the lungs (target organ for acute exposure), the eyes (affected by chronic exposure), and the skin (since mercury is a known skin sensitizer). Early signs and symptoms of mercury intoxication were elicited by employing finger-to-nose testing, rapid alternating hand movements, and diminished two-point discrimination tests.

The guidelines used to interpret the significance of an individual’s results were the following.

1. If a person’s laboratory results were less than 1 µg/g, they were told that the Hg level in their hair was below the recommended upper limit. The United States Environmental Protection Agency (EPA) [18] recommends that safe levels of Hg found in hair are below 1 µg/g.

2. If a person’s laboratory results were between 1 µg/g and 11 µg/g, they were advised that their Hg level was above the recommended limit. They were also told that they could be at elevated risk if they were pregnant, planning to become pregnant, or nursing a baby. They were advised to seek the advice of a medical professional if they had any health concerns.

3. If a person’s laboratory results were greater than 11 µg/g, they were told that their Hg level was above the benchmark dose set by the EPA. They were also told that they could be at elevated risk if they were pregnant, planning to become pregnant, or nursing a baby. They were advised to seek the advice of a medical professional.

Regardless of the other languages understood by the people in (Apetina) and (Anapayke), that is, Dutch and Sranan Tongo, they assert that they are only able to fully understand public health information when the material is translated into their native Wayana language. As a consequence of this observation, the communities are currently working with Stichting Wadeken Wasjibon Maria, with support from the Suriname Indigenous Health Fund, to develop more detailed education programs that explain the importance of the guidelines for pregnant women and children in the Wayana language.

2.3. Data Analysis. In this study, hair mercury results were summarized using simple descriptive statistics including arithmetic mean, median, standard deviation, and range. The mean hair concentrations were evaluated by population, age and gender using the two-tailed t-test assuming equal variances (P < 0.05). Geometric mean and standard deviation were used for the analysis of exponential data related to risk.
Table 1: Total hair mercury (Hg) concentrations (µg/g) and risk by population (community) and subgroup (age and gender) among residents of Puleowime (Apetina) and Kawemhakan (Anapayke).

<table>
<thead>
<tr>
<th>Community/age group</th>
<th>Average age</th>
<th>No.</th>
<th>Geometric mean Hair Hg (µg/g) ± SD</th>
<th>Median hair Hg (µg/g)</th>
<th>Hazard quotient (HQ)</th>
<th>Range hair Hg (µg/g)</th>
<th>Geometric mean of individual risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puleowime (Apetina)</td>
<td>24</td>
<td>158</td>
<td>14 ± 6</td>
<td>14</td>
<td>6.0</td>
<td>3–34</td>
<td>0.23</td>
</tr>
<tr>
<td>≤5 years</td>
<td>3</td>
<td>23</td>
<td>17 ± 7</td>
<td>20</td>
<td>7.0</td>
<td>5–28</td>
<td>0.25</td>
</tr>
<tr>
<td>Male</td>
<td>2</td>
<td>9</td>
<td>20 ± 6</td>
<td>23</td>
<td>9.0</td>
<td>7–28</td>
<td>0.45</td>
</tr>
<tr>
<td>Female</td>
<td>16</td>
<td>14</td>
<td>15 ± 7</td>
<td>16</td>
<td>6.0</td>
<td>5–26</td>
<td>0.18</td>
</tr>
<tr>
<td>6–14 years</td>
<td>9</td>
<td>53</td>
<td>14 ± 5</td>
<td>14</td>
<td>6.0</td>
<td>6–34</td>
<td>0.26</td>
</tr>
<tr>
<td>Male</td>
<td>9</td>
<td>27</td>
<td>16 ± 6</td>
<td>15</td>
<td>7.0</td>
<td>8–34</td>
<td>0.42</td>
</tr>
<tr>
<td>Female</td>
<td>10</td>
<td>26</td>
<td>13 ± 5</td>
<td>14</td>
<td>6.0</td>
<td>6–25</td>
<td>0.15</td>
</tr>
<tr>
<td>15–25 years</td>
<td>20</td>
<td>19</td>
<td>14 ± 7</td>
<td>14</td>
<td>6.0</td>
<td>6–32</td>
<td>0.16</td>
</tr>
<tr>
<td>Male</td>
<td>22</td>
<td>5</td>
<td>13 ± 5</td>
<td>14</td>
<td>6.0</td>
<td>6–18</td>
<td>0.20</td>
</tr>
<tr>
<td>Female</td>
<td>19</td>
<td>14</td>
<td>14 ± 8</td>
<td>13</td>
<td>6.0</td>
<td>8–32</td>
<td>0.15</td>
</tr>
<tr>
<td>26–45 years</td>
<td>35</td>
<td>35</td>
<td>15 ± 7</td>
<td>14</td>
<td>6.0</td>
<td>6–33</td>
<td>0.22</td>
</tr>
<tr>
<td>Male</td>
<td>35</td>
<td>13</td>
<td>15 ± 8</td>
<td>13</td>
<td>6.0</td>
<td>7–33</td>
<td>0.27</td>
</tr>
<tr>
<td>Female</td>
<td>34</td>
<td>22</td>
<td>14 ± 7</td>
<td>15</td>
<td>6.0</td>
<td>6–30</td>
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<tr>
<td>&gt;45 years</td>
<td>59</td>
<td>28</td>
<td>13 ± 6</td>
<td>13</td>
<td>6.0</td>
<td>3–29</td>
<td>0.22</td>
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<tr>
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<td>11 ± 6</td>
<td>13</td>
<td>5.0</td>
<td>3–29</td>
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<tr>
<td>Female</td>
<td>62</td>
<td>15</td>
<td>14 ± 5</td>
<td>14</td>
<td>6.0</td>
<td>7–27</td>
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<tr>
<td>Population risk</td>
<td></td>
<td>93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kawemhakan (Anapayke)</td>
<td>28</td>
<td>106</td>
<td>9 ± 4</td>
<td>9</td>
<td>4.0</td>
<td>2–19</td>
<td>0.01</td>
</tr>
<tr>
<td>≤5 years</td>
<td>3</td>
<td>17</td>
<td>9 ± 4</td>
<td>10</td>
<td>4.0</td>
<td>2–18</td>
<td>0.02</td>
</tr>
<tr>
<td>Male</td>
<td>3</td>
<td>9</td>
<td>8 ± 3</td>
<td>10</td>
<td>4.0</td>
<td>2–14</td>
<td>0.01</td>
</tr>
<tr>
<td>Female</td>
<td>3</td>
<td>8</td>
<td>10 ± 4</td>
<td>9</td>
<td>4.0</td>
<td>6–18</td>
<td>0.02</td>
</tr>
<tr>
<td>6–14 years</td>
<td>9</td>
<td>27</td>
<td>5 ± 2</td>
<td>6</td>
<td>2.0</td>
<td>2–9</td>
<td>0.00</td>
</tr>
<tr>
<td>Male</td>
<td>9</td>
<td>13</td>
<td>6 ± 2</td>
<td>5</td>
<td>3.0</td>
<td>3–9</td>
<td>0.00</td>
</tr>
<tr>
<td>Female</td>
<td>9</td>
<td>14</td>
<td>5 ± 2</td>
<td>6</td>
<td>2.0</td>
<td>2–8</td>
<td>0.00</td>
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In this report, the concept of a benchmark dose (BMD) is used to calculate risk. The BMD is the estimated dose corresponding to a specified incremental risk over and above background. Individual risk, defined here as the probability of having a 5% chance of exhibiting an adverse neurological effect, was based on the most conservative of the three dose response functions (DRFs) reported by Sullivan et al. [19] in which risk is correlated to the biomarker of Hg concentration in hair as a function of the amount of Hg consumed through fish. According to Sullivan, the probability of having a 5% chance of exhibiting an adverse neurological effect was estimated to be 0 for hair at 0–3 ppm Hg, $1 \times 10^{-2}$ for hair at 4 ppm, $1 \times 10^{-3}$ for hair at 5-6 ppm, $2 \times 10^{-3}$ for hair at 7 ppm, $3 \times 10^{-3}$ for hair at 8 ppm, $5 \times 10^{-3}$ for hair at 9 ppm, $1 \times 10^{-2}$ for hair at 10 ppm, $1 \times 10^{-1}$ for hair at 11 ppm, $4 \times 10^{-1}$ for hair at 12 ppm, $6 \times 10^{-1}$ for hair at 13 ppm, and $9 \times 10^{-1}$ for hair over 13 ppm. Population risk was obtained through the summation of risk for all individuals [19, 20]. Risk assessors use the term “population risk” to mean the number of people in the community that are affected. By contrast, “individual risk” is the incremental probability that the hazard will impose an effect on some particular person [21].

2.4. Hazard Quotient. Exposure can be expressed as a non-carcinogenic risk expressed in terms of the hazard quotient.
Methodologically, outside experts became learners, facilitators, and catalysts in a process that gathered momentum as the community came together to analyze and discuss the research process and the results it yielded. The process was characterized by a cycle of dialogue, reflection, and action. This method relied less on the methodological framework than it did on the relationship between the researchers and the community. The program was managed in a manner that ensured that all partners’ interests and aspirations were considered, and activities were implemented only with agreement from all partners involved. The relationship followed here was described by Biggs [26] who described this mode of community participation as collegiate where researchers and local people work together as colleagues with different skills to offer, in a process of mutual learning where local people have control over the process.

2.6. Human Subjects Review. The SIHF research team consulted with the human subjects review staff at the University of Washington who approved the project plan on 18 June 2007 and again on 30 December 2010 to review plans to publish this paper. The Institutional Review Board staff found that the research design did not require full IRB review since the traditional roles of researcher and research subject do not apply. Since research subjects were co-investigators leading the research process while the western research team acted as consulting technicians, informed consent was deemed unnecessary.

3. Results

The estimated risk of adverse neurological effects at measured levels of Hg in hair are given in Table 1. In both communities, 58% of the people who submitted hair samples had Hg levels above the World Health Organization [27, 28] safety limit (10 µg/g). The mean hair Hg concentration in Puleowime (GM = 14) was significantly higher (P < 0.05, df 262) than the hair Hg levels in Kawemhakan (GM = 8). Although mean hair concentrations varied from 11 ± 6 to 20 ± 6 µg/g, the differences were not significant at the 95% confidence level (Table 2). The population

<table>
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risk for Puleowime was 93 and for Kawemhakan was 18, which reflects the number of people in each community expected to be affected by exposure to excess levels of mercury.

Facilitators from SWWM also noted information related to fish consumption patterns and self-reported symptoms. In Puleowime, all participants reported eating fish at least 3 times per day every day whereas, in Kawemhakan, more than 25% of the participants reported consuming fish less frequently. Residents in Puleowime (Apetina) and Kawemhakan (Anapayke) reported that the two most common varieties of fish eaten in their communities were anumara (Hoplias spp.) and tucunare (Cichla sp.).

Among participants in Puleowime, 12% reported feeling numbness in arms, fingers, or toes. In Kawemhakan, that number was higher at 36%. Three women with hair mercury levels between 25 and 30 µg Hg/g requested a health assessment. All complained of headaches and pain and tingling in their hands and feet. The attending physician, D. J. Roesel, Clinical Assistant Professor, General Internal Medicine and Adjunct Clinical Assistant Professor, Global Health at the University of Washington, noted that three women who presented themselves to him with concerns that they were affected by exposure to mercury exhibited abnormal neurological testing, with poor performance on finger-to-nose testing, rapid alternating hand movements, and diminished two-point discrimination. In both Puleowime and Kawemhakan, over one-third of the participants complained of either headaches or strong feelings of sadness or depression at least once weekly.

4. Discussion

This study was successful in reaching its primary objective. Two Wayana communities in southeast Suriname successfully completed a project in which they measured for themselves their risk of exposure to mercury (Hg) contamination using a model of community-led research.

Mercury exposure in the Wayana villages of Puleowime (Apetina) and Kawemhakan (Anapayke) appears to mirror the problems documented elsewhere in the region. In two Wayana villages in French Guiana, 58% and 57% of the people had Hg levels above the World Health Organization (WHO) safety limit (10 µg/g), respectively [27, 28]. Frery et al. [11] measured hair Hg concentrations in 235 samples from people in four villages along the upper Maroni River in French Guiana where the average concentration was 11 ± 4 µg/g (mean ± SD). This value corresponds to the exposure levels in Kawemhakan where the average hair Hg concentration was 8 ± 4 µg/g. In Puleowime, however, the average hair Hg concentration was significantly higher at 14 ± 6 µg/g (P < 0.05).

Frery et al. [11] conducted a detailed familial dietary study associated with Hg measurements in fish and some game. The Frery study was conducted over 7 days in two different seasons in the four most populated Wayana villages on the upper part of the Maroni River. The results confirm mercury exposure of the Wayana population related to a diet rich in fish, which are highly contaminated for certain species (up to 1.62 mg/kg fresh weight or 8.1 mg/kg dry weight in skeletal muscle). Frery showed that Hg concentrations in fish muscle were closely linked to the feeding regime and position of fish in the food webs. Overall, 14.5% of the fish collected exceeded the 0.5 mg/kg (fresh weight) safety limit. Four carnivorous species accounted for no less than 72% of the metal ingested by the Wayana families, although these represented only 28% of the consumed fish biomass. The species were Pseudoplatystoma fasciatum (27% of the Hg dietary intake), Hoplias aimara (27%), Ageneiosus brevifilis (11%), and Serrasalmus rhombeus (6.5%). Cynodon meionactis, which along with P. fasciatum has the highest Hg concentrations, was hardly eaten at all (especially by children) because these fish contain a large number of bones.

The two species that are consumed in the greatest amounts, Myleus rhomboidalis/tometes (12.7%) and Doras micropus (11.2%), are not contaminated to a very high degree (100 and 1,160 (micro) g/g, dw, resp.). The Frery study revealed excessive exposure to mercury in the Wayana population was related to the consumption of contaminated fish.

While several studies have shown that Hg levels in hair are higher in residents of areas contaminated by mercury than in residents of uncontaminated regions, others show wide variations depending on the relative importance of fish in the diet [5]. In Puleowime, the community fills more of its dietary needs by fishing than Kawemhakan where the residents are more acculturated and have a more diversified diet. In both cases, subsistence fishers consume large amounts of fish and represent high exposure cases that form the tail of the distribution of the general population. The Wayana live in isolated villages on the Tapanahoni River (Apetina) and the Lawa River (Anapayke) and are considered excellent examples of members of a “fishing civilization.” Recent investigations by Frery et al. [11] show that most subjects take more than 14 fish meals per week. The actual exposure, therefore, among these populations will be highly variable, location specific, and they will depend on local fish Hg levels and individual fish consumption patterns.

In both Puleowime and Kawemhakan the risk of having an adverse effect is quite large (population risk 93 and 18 resp.). In general, a lifetime risk of one-in-ten-thousand and in some instances one-in-one million has become a common place standard in public health discourse and policy. The risks for subsistence fishers in Puleowime and Kawemhakan are orders of magnitude greater than the risk that is acceptable in mainstream society.

Another way to consider risk is by comparing the estimated oral exposure dose (µkg/kg/d) to an oral reference level to calculate the hazard quotient (HQ) [23–25]. For Puleowime, the dietary exposure rate was 1.4 µkg/kg/d and for Kawemhakan, 0.9 µkg/kg/d. The FAO/WHO Expert Committee on Food Additives (JECFA) reference level for dietary exposure to Hg is 2.3 µkg/kg/d [22]. Both yield hazard quotients greater than 1 as did the individual exposure doses based on measured hair Hg concentrations (Table 1). Of these, approximately 15% were children under the age of 5 and 34% were women of childbearing age. These people are especially susceptible to mercury exposure because of the...
sensitivity of the developing nervous system in the fetus and in children.

From the point of view of the physician who was in attendance, there are many potentially confounding factors that are affecting community health. As a global and public health professional, the research team physician struggled with the idea that, although there are compelling instances of high levels of mercury exposure, there was no “smoking gun” in terms of clearly caused, well-documented health impacts from mercury exposure. The health impacts observed can also be related to social decay, loss of hunting grounds and land rights, and the threat of extinction of these indigenous communities and their way of life. Consequently, when considering the impacts of contamination from mining it is important to consider the broadest definition of “health” possible [23, 24]. This approach argues in favor of long-term community partnerships over short-term public health campaigns that are iterative in nature and open to the possibility of collaboration with other disciplines that can address a broader range of social and legal considerations.

5. Wayana Community Review of Report

Research data on the exposure of Wayana people to mercury has been reported since before 1994 [7]. Since then, research and outreach has been conducted by government and non-government organizations including a study conducted in 2004 by the World Wildlife Fund. As late as 2007, the results of this research had not been published nor returned to the Wayana communities.

There were two ways in which the community-led approach to research was different from research performed previously among the Wayana. The first was that the Wayana communities were equal partners with Western-trained experts. The community-led approach involved a collaboration of “formally trained research” partners from the fields of environmental toxicology, sociology, and public health as well as indigenous advocates and community leaders. As the experts in their environmental and cultural context, community leaders were able to identify the research question, select a feasible and culturally appropriate research strategy, interpret data findings within their own social structure, and identify next steps within traditional decision making mechanisms. Second, instead of creating knowledge for knowledge’s sake or instead of performing research for the advancement of the field of risk assessment or toxicology, the community-led approach was an iterative process that incorporated research, reflection, and action in a cyclical process for the benefit of the communities at risk.

According to Aptuk Noewahé, the Wayana Gramman (leader) from Puleowime (Apetina), past research was conducted by scientists who, “came often, said big things, made promises, then left.” He said that if scientists want to help, then they should “include the community, listen and help. Otherwise, they should just go away”. As Cornwall and Jewkes [17] argue “participatory research consists less of modes of research which merely involve participation in data collection than of those which address issues of the setting of agendas, ownership of results, power and control.”

After the risk assessment analyses were complete, the results were discussed with the community. The communities asked Suriname Indigenous Health Fund and Stichting Wajibon Wadeken Maria to help write this report communicating results of the community-directed risk assessment. The report was drafted in English, translated into their native language (Wayana), and reviewed. Regardless of the other languages understood by the people in Puleowime and Kawemhakan they were only able to fully understand the details of this complex problem when the report was translated into their native language for their review, comment, and approval. As a consequence of this process, the communities now want to repeat the education programs presented previously by government and NGOs, this time in their Wayana language.

Noewahé added that, “We support the article and the research because we led the process as partners in the project, and we are involved. Usually people do not discuss their work with us, not even the results of their work. This article is important because our problem needs to be known by others. Also, we look forward to continuing this project and we hope that together we can work towards a sustainable solution to our problem together with the government and other health organizations.”

Community elders agreed that, “this was a good project, because it means our children could have a good future.” However, there were a lot of other comments that were detailed in nature and reflected the complexity of the problem. The first was language. As a consequence of engaging the community in the conduct of this risk assessment project and discussing the data and drafts of this manuscript in the community’s native Wayana language, one participant noted that, "Now we understand the problem and want to repeat the education programs presented previously by the government and NGOs, this time in our Wayana language.” Residents challenged suggestions made by Westerners that communities impacted by mercury (Hg) contamination must eat small, young fish from the lowest possible trophic level; residents noted they do not often have a choice. “We eat what the river gives us. We tried eating only the fish we were told to eat but could not catch enough and after 3 or 4 months we had to quit trying.” Instead, communities want to focus on integration, education, land rights, human rights, and the root causes leading to a wider range of problems that includes risk from exposure to mercury.

Community leaders identified three major priorities for further investigation. First, the Wayana communities of Puleowime (Apetina) and Kawemhakan (Anapayke) prioritized the assessment of potential health impacts from Hg exposure. Health assessments must be conducted for all community residents, beginning with the most susceptible subpopulations. Second, further risk assessments to evaluate the degree and frequency of exposures above the reference level must be conducted since residents of these communities consume larger amounts of fish than mainstream communities. Third, the major concerns facing the communities voiced throughout the research process that were not addressed in this study must be addressed. These include the encroachment of their traditional homeland by
miners who are heavily armed and prevent villagers from hunting, fishing, and providing for their families; and the scarcity of clean water for drinking, cooking, and bathing due to contamination from mining.

On its own, a risk assessment study can serve as an example of reductionism and illustrates the approach that forms the basis for modern science. In many cases, a good understanding of the components of a system will lead to a good understanding of the system as a whole. However, within the context of an indigenous society where the relationship between the environment and human population is complex and multilayered, emergent properties of the system are impossible to predict from knowledge of discrete parts, and a holistic rather than a reductionist approach is necessary. The community-led research process provides a method for bridging the disciplines within scientific paradigms with traditional indigenous paradigms. The Wayana have a cosmology, which is distinct from the Western Reductionist approach to science. It integrates society, nature, and health and has more in common with Western Complexity theory, systems thinking and a holistic paradigm. By allowing community members to take a lead role in the research process, community-led research facilitates the exchange of information and shared decision-making that provides access to public health information for both at-risk communities and researchers.

6. Conclusion

In this study the Wayana communities of Puleowime (Apetina) and Kawemhakan (Anapayke) in Suriname identified for themselves that they were at a high lifetime risk of adverse effects from exposure to mercury. Exposure was higher in Puleowime (Apetina) compared to Kawemhakan (Anapayke) where differences in the relative importance of fish in the diet may be responsible. Risk estimates suggest that all participants in the study exceeded the one-in-a-hundred-thousand policy common in mainstream society.

The community-led research process allowed community leaders to identify the research question most meaningful to them, select a feasible and culturally appropriate research strategy with the assistance of trained experts, collect data from participants within their community themselves, interpret data findings within their own social structure, and identify next steps within traditional decision-making mechanisms.

The community-directed approach increases the visibility of researcher and the transparency of their intentions, which are significantly greater than in conventional research. In practice, community-directed research was not a simpler alternative to a conventional research project and working in collaboration with local people is far from easy. Contrary to expectations, control over research does not devolve completely onto the community, nor do communities want to assume complete control.

Acknowledgments

This paper was prepared by the authors at the request of Aptuk Noewahé, the granman from Puleowime (Apetina) and Amaiopoti, granman from Kawemhakan (Anapayke). Drafts were translated by Leon Eric Wijngaarde, Sita Tempio, and Eveline Monsanto, all from Stichting Wasjibon Dadeneken Maria, and reviewed with community members who contributed comments and approved the final draft. Financial support for this project was provided through an International Engagement Award from Wellcome Trust (089659/Z/09/Z).

References


Research Article

Evaluation of Trace Metal Levels in Tissues of Two Commercial Fish Species in Kapar and Mersing Coastal Waters, Peninsular Malaysia

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This study is focused on evaluating the trace metal levels in water and tissues of two commercial fish species Arius thalassinus and Pennahia anea that were collected from Kapar and Mersing coastal waters. The concentrations of Fe, Zn, Al, As, Cd and Pb in these coastal waters and muscle, liver and gills tissues of the fishes were quantified. The relationship among the metal concentrations and the height and weight of the two species were also examined. Generally, the iron has the highest concentrations in both water and the fish species. However, Cd in both coastal waters showed high levels exceeding the international standards. The metal level concentration in the sample fishes are in the descending order livers > gills > muscles. A positive association between the trace metal concentrations and weight and length of the sample fishes was investigated. Fortunately the level of these metal concentrations in fish has not exceeded the permitted level of Malaysian and international standards.

1. Introduction

It is unfortunate that we, human beings without realizing the consequences of pollution, do a lot of activities that terribly ruin the nature, resulting in the denial of healthy environment to our successors. Water contamination is one of the serious concerns that affect the marine ecosystem with high concentration of trace level metals. Malaysia is one of the countries that critically face this issue since 1990. The reason for this alarming situation is due to the rapid economic growth that the country is experiencing for the past two decades. The contamination of water cannot be taken as price for this economic boom.

According to Paquin et al. [1] the coastal or river waters are contaminated by the dumping of industrial wastages. The metals accumulated in these waters infect the humans by direct consumption of water or through consuming the affected organisms like fishes [2, 3] claim that when the level of trace metal concentrations exceeds the stipulated level, it turns out to be toxic. Very recently, the work in [4] has stated that the higher level of metal concentration will bring shattering effect to the ecological balance by altering the range of organisms in water.

Several researchers, including [5–8], have studied the importance of fishes and their healthy benefits. They claim that fishes are the most healthy food with the high source of omega 3 fatty acids, that brings a lot of benefits to us, including the reduction of heart-related diseases. Apart from this, the fishes are rich source of vitamins, minerals, and proteins. Studies in [9, 10] reveal that 60 to 70% of protein needs are fulfilled by the consumption of fishes in Malaysia. But, [11–13] have analysed the other side of high fish consumptions. They claim that other than cardiovascular benefits, the exceeding level of fish diet brings negative impact to the human society.

Researches in [14, 15] reveal that iron and zinc are essential for the metabolism of fishes. At the same time, aluminium, cadmium, arsenic, and lead are added to the food chain...
of these organisms though they do not play any important role in the metabolic activities. Whereas [16] ascertain that when we consuming fishes with high accumulation of these metals, over a long period of time, will bring harmful effects to us. Reilly and Barton [17, 18] added that the continual high dosage of Al consumption will result in lung fibrosis, osteomalacia, defective bone mineralization, dialysis dementia, and ferric-independent microcytic anaemia. Further studies regarding diseases related to high dose of mineral consumption can be summarized as follows. High Cd Accumulation brings skeletal damage, kidney dysfunction, and reproductive deficiencies [19]; cardiovascular disease, skin disorders, cancer, and neurotoxicity are triggered by arsenic consumption [20]; Pb, termed as neurotoxins, brings cardiovascular diseases to adults and reduced mental development in children [19, 20].

According to Canli and Atli [21] Fe and Zn are very vital for the normal metabolism for the schools of fishes. At the same time iron is one of the important trace metals that highly benefits humans. It serves as the oxygen conductor between the tissues and lungs. Camara et al. [22] have established the health benefits of advocated level of mineral consumption. They claim that deficiency of Zn will cause loss of appetite, growth retardation, skin changes, and immunological abnormalities. But Tüzen [23] has stated that though Zn has biological significance, excessive consumption of these kinds of metals will affect the humans. The trace metal sewage from industries pollutes water and fishes in turn. The consumption of the affected fishes over a prolonged period will harm the health of humans.

Fortunately previous studies reveal that the trace metal concentration level in fishes is not that much alarming in South East Asian countries. The researchers have examined muscles, livers, and gills of fishes as these organs play different roles in bioaccumulation process [24]. Hamilton and Mehrle [25] say that the concentration level of metals in gills represents the level of metals in water, where they dwell. The concentrations of metals in liver represent their storage level. Metallothioneins (MTs) are the metal-binding proteins accumulated in livers, whereas [26, 27] assert that metal accumulation in the muscles of fishes is dangerous as they are the most edible part. They also established that, environmental evaluation in aquaecology shall be conducted in water, organisms, or sediments. Each of these components provides partial image of metal accumulation in the whole ecosystem.

According to Marcovecchio and Moreno [28], studying the trace level in organisms reflects the real degree of pollution in the related environment. References [29–31] state that generally fishes are used as the medium for monitoring anthropogenic pollution level in the environment. As fishes are the last level of the food chain, the polluted varieties will easily pass the metals into the humans when they are consumed [32–35].

The marine ecosystem of Kapar is selected as it is located in the Strait of Malacca which consists of many pollution sources situated around it. This locality gets infected by a great variety of pollutants due to the existence of large number of international shipping lanes and the concentration of agriculture, industrialization, and urbanization activities along the coast of Peninsular Malaysia [36]. Moreover, the Strait of Malacca is one of the most vulnerable areas to contamination by oil spills [37]. On the other hand, the Strait of Malacca is the most important fishing ground in Malaysia, accounting for approximately 70% of total fish landings of the country [37].

Apart from the above-mentioned sources of pollution, an electric power station that uses coal and discharges the polluted, preused water into the surface water systems surrounding Kapar, also contribute to the trace metal pollution of the marine ecosystem in this area. Moreover, Kapar has great importance for the local fishery industry therefore, it is vital to estimate the selected metals in fish of the Kapar coastal water, to define the current trace metal levels in the fish as well as to monitor the trends of change in fish trace metal levels with time.

However, evaluation of the levels of the same metals in Mersing allows for comparison between the two areas, particularly in terms of the kinds and effects of different pollution sources in the two areas. This study is focused on measuring the concentration level of selected metals (Al, Fe, Zn, As, Cd, and Pb) in the muscles, livers, and gills of selected species of fishes and the pollution level in the coastal areas in Malaysia. Moreover, the relationships between the trace metal levels in these tissues and the length and weight of fishes were also investigated.

2. Materials and Methods

2.1. Reagents. The reagents with suprapur quality, analytical grade Nitric acid (65%), and hydrogen peroxide (30%) were acquired from Merck (Darmstadt, Germany) along with the stock standard solutions of Al, Fe, Zn, As, Cd, and Pb in concentrations of 1,000 mg/L. Prior to the experiments the apparatus were sterilised by soaking them overnight in diluted nitric acid (10%) and were later rinsed with distilled deionised water. The experiments were conducted using the distilled deionised water.

2.2. Apparatus. In this study we have used Perkin Elmer model Elan 9000 inductively coupled plasma mass spectrometry (ICP-MS, USA) [40]. After calibrating the instrument with standard solutions derived from commercial materials, it was optimized according to the manufacturing standards. Besides these initiations, the cones and tubes were thoroughly cleaned to get rid of any possible residues. Table 1 shows the analytical conditions for determining the trace metals by the inductively coupled plasma mass spectrometry (ICP-MS).

2.3. Study Area. Water and fish sampling were done at two different stations of coastal waters of Peninsular Malaysia in October 2009. Stations shown on the map (Figure 1) were chosen in relation to the contamination gradient.

The first station chosen was Kapar (3°11′54″ N, 101°32′66″ E) located in Selangor on the west coast of Peninsular Malaysia near the Sultan Salahuddin Abdul Aziz Power Plant
station. In terms of pollution, the water quality of Kapar coast is influenced by various industrial outputs, discharged directly to the sea or by rivers. The second station was Mersing (2°25’60” N, 103°49’60” E) in Johor on the west coast of Peninsular Malaysia, it is relatively clean when compared with Kapar.

2.4. Samples Collection and Samples Preparation

2.4.1. Collection of Water Samples. For research purpose a stint of 200 ml of water was collected with the help of 21 cc capacity automated sampler. The sample was collected from the surface of the coastal water (depth range < 10 centimetre). The sample was then filtered using Whatman 0.45 µm membrane filter paper, and filled in polyethylene bottles (amber coloured). These bottles were pre washed with 1 (N) HNO₃ and deionised water. Later 3 mL of concentrated HNO₃ was added to the collected sample to avoid oxidation and preserved at 4°C, prior to analysis.

2.4.2. Collection of Fish Samples. Two commercially significant and nutritious fish species, namely, duri (Arius thalassinus) and gelama (Pennahia anea), were selected and collected with various fishing methods by fishermen (Table 2). Ten fresh fish specimens of both the species, from each station, were collected from local fishermen. The samples were stored in a cool box (−4°C) and transported to the laboratory for metal analysis. Total length (cm) and weight (g) of the fish samples were measured before dissection.

The specimens were dissected with sterilized stainless steel equipment. The dissected parts such as muscle, liver, and gills were later dried in an oven at 80°C until constant weight was obtained. The homogenized samples (muscle, liver, and gills) were digested in triplicate in a microwave oven digestive system (Start D Microwave Digestive System) with HNO₃ (65% Merck) and H₂O₂ (30% Merck) in Teflon vessels. The residues were filtered through 0.45 µm Whatman filter paper (Whatman international Ltd. Cat) and transferred to a 50 mL volumetric flask and diluted to level with deionised water in the case of muscle and gills. However, in the case of liver tissues, the final dilution volume was 25 mL rather than 50 mL [41].

Analytical blanks were run in the same way as the samples and determined using standard solutions, prepared in the same acid matrix. All chemical materials and standard solutions used in this study were obtained from Merck and were of analytical grade.

2.5. Analysis of Metals. As discussed earlier in Section 2.2, the concentrations of iron (Fe), zinc (Zn), aluminium (Al), arsenic (As), cadmium (Cd), and lead (Pb), in water and two species of fish, were examined using the inductively coupled plasma mass spectrometry. The analytical findings were articulated in terms of micrograms of metal in every gram of fish on dry weight basis (µg/g dry weight). The performance assessment of this method was done by examining a standard reference material of marine biota sample (SRM2976, freeze-dried mussel tissue, National Institute of Standards and Technology, USA).

2.6. Statistical Analysis. Due to the lack of normal distribution of data, the log transformation was implemented for the normalization process. To examine the vital differences in the concentrations of heavy metals in the two research sites,
the t-test was conducted. Moreover, to investigate the denoting dissimilarity of concentrations of trace metals among the three fish organs, the Kruskal-Wallis test was used. Pearson rank correlation analysis was employed, to measure the latent associations of metal concentrations with fish weight and length. For which a P value less than 0.05 was considered as suggestive of statistical significance. SPSS for windows, version 16.0 was used to perform all the above-mentioned tests.

### 3. Results and Discussion

#### 3.1. Validation of Analytical Methods

The precision and accuracy of the applied analytical method was validated by accurate analysis of standard reference material of marine biota sample (SRM2976, freeze-dried mussel tissue, National Institute of Standards and Technology, USA). All the runs were carried out in triplicate. The results obtained on the SRMs are shown in Table 3 which was in a good agreement with the certified values for all metals. Recovered values of all metals were between 83% and 109% of the certified value.

#### 3.1.1. Quality Control

It is vital for the analytical instruments (ICP-MS) to meet the standard before it can produce a reliable data. Calibration curve of each element must be able to produce good correlation coefficient $r^2 = 0.999$.

#### 3.1.2. Instrument Detection Limit (IDL)

The IDL is the smallest signal that can be differentiated from background noise by a specific device. The method detection limit should be always higher than the IDL, whereas the IDL is thrice equal to the standard deviation of 10 replicates measurements of calibration blanks signal at the selected elements.

#### 3.1.3. Limit of Detection (LOD)

The LOD is the least amount of a substance that can be distinguished from the absence of it (a blank value) within a stated confidence limit (generally 1%). The method detection limit is defined as the concentration corresponding thrice to the standard deviation of ten reagent blanks [42]. Table 4 shows the method detection limit ($\mu$g/g) of five metals and the FDA recommended health-criteria concentrations ($\mu$g/g) of five metals in seafood [38, 39]. The detection limit values were found to be 0.287 $\mu$g/g for Al, 0.492 $\mu$g/g for Fe, 0.474 $\mu$g/g for Zn, 0.403 $\mu$g/g for As, 0.193 $\mu$g/g for Cd, and 0.606 $\mu$g/g for Pb which were much lower than the recommended health-criteria values.

#### 3.1.4. Limit of Quantitation (LOQ)

The LOQ is mathematically expressed as equal to 10 times the standard deviation of the results for a sequence of replicates used to establish a reasonable boundary of detection. The LOQ values were found to be 2.87 $\mu$g/g for Al, 4.92 $\mu$g/g for Fe, 4.73 $\mu$g/g for Zn, 4.03 $\mu$g/g for As, 1.95 $\mu$g/g for Cd, and 6.16 $\mu$g/g for Pb.

#### 3.2. Trace Metals Contents in Water

Analysis on water quality of baseline study for Kapar and Mersing seawater are necessary to predict the level of pollutant as well as to the environment in the study areas. Table 5 shows the water temperature, pH, dissolved oxygen (DO), and the trace metal levels of baseline study for Kapar and Mersing seawater are necessary to predict the level of pollutant as well as to the environment in the study areas. The water temperature from Mersing and Kapar ranges from 19.6 to 22.5 °C; the variation in water temperature was mainly due to prevailing weather conditions. The statistical analysis showed that there was no significant difference between the two locations ($P > 0.05$). Moreover, the pH has ranged between 7.23–7.56. The standard pH for seawater is 6.5–8.5 [43], and the values obtained were within the recommended standard, and there was no significant difference in pH for the two sampling sites. The lowest dissolved oxygen (DO) value recorded was 4.37 mg/L at Kapar, while the highest was 7.90 mg/L at Mersing. Generally, the dissolved oxygen will be affected by water temperature, tides, and depths. Furthermore, the maximum concentration of the metals in the water samples in the descending order were Fe > Al > As > Zn > Pb > Cd and Fe > As > Cd > Zn > Al > Pb from Kapar.
and Mersing, respectively. Al, Zn, and As had higher concentration in Kapar, whereas the Fe and Cd had higher in Mersing. There was no significant difference in metal concentrations in the two sampling locations. Additionally, the comparison of trace metals level with NWQSM and WHO [44, 45] showed that all the metal concentrations were below the maximum acceptable concentration (MAC), except for Cd from both sites that showed high levels exceeding the international standards suggesting that adverse effects to aquatic organisms would frequently occur.

3.3. Trace Metals Contents in Various Organs in Fish. Knowledge about heavy metals concentration in fish is important with respect to nature management and human consumption. Levels of six metals (µg/g dry wt.) in muscle, liver, and gill tissues of two fish species collected from the coastal waters around Kapar and Mersing are shown in Tables 6 and 7. Generally, the highest concentrations of iron, zinc, aluminium, arsenic, and lead were found in the liver tissues of both examined fish species. The analysis of variance proved that the mean concentrations of metals in the organs of each species were significantly different \( (P < 0.05) \) in both the species except for Cd. The concentrations of the studied metals decreased in the following order Fe > Zn > Al > As > Pb > Cd in the two species. Iron exhibited the highest concentrations in all the examined organs of both species, followed by Zn. On the other hand, the levels of Pb and Cd were generally the lowest. Similar findings were reported by many researchers [14, 46–48].

It is observed that Fe concentration was the highest in both species and both study areas. In the present study, with the exception of Al, liver had significantly higher trace element concentrations than gills and muscle. It is observed that the mean concentrations of metals in the muscle, liver, and gills of each fish species showed great variations, this may be related to the differences in ecological needs, swimming behaviours, and the metabolic activities among different fish species.

The differences in metal concentrations of the tissues might be due to their capacity to induce metal-binding proteins such as metallothioneins. Our study showed that the metal levels in liver and gills were highest in the sampled species. It is well known that large amount of metallothioneins induction occurs in the liver tissue of fishes. The adsorption of metals onto gill surface could also be an important influence in total metal levels of the gill [30].

The mean concentrations of Fe in the muscles of P. Anea and A. thalassinus in Kapar were 34.91 µg/g and 53.84 µg/g,
respectively. However, in Mersing the mean concentrations were 21.47 µg/g in P. Anea and 21.62 µg/g in A. thalassinus. It is revealed that Fe concentrations varied significantly (P < 0.05) between the two stations. Higher Fe concentration in muscles of both species was found in the fish from Kapar than that of Mersing. The reason for this is that the Kapar area is polluted by various sources such as electrical power station, international shipping activities, and urban and agricultural activities. Similarly, the concentrations of Fe in the liver tissues of P. anea and A. thalassinus in Kapar were, approximately, 1976.0 µg/g and 1008.0 µg/g, respectively. But in the same tissues of the fish from Mersing the concentrations were 526.0 µg/g and 924.6 µg/g, respectively. The levels of iron in the muscles of Mediterranean Sea fish that are reported in the literature ranges from 59.6 and 73.4 µg/g [31]. The concentrations of Fe in the fish muscle were reported to have the range of 24.1–50.3 µg/g in Parangipettai Coast, India [49] and the range of 49.9–889 µg/g in the Turkish seas [47]. Therefore, the levels of iron in the fish muscles reported in this study are generally in accordance with the literature.

According to the results (Tables 6 and 7), concentrations of Zn in the livers of P. anea and A. thalassinus collected from Kapar and Mersing were 114.1 µg/g and 555.9 µg/g (Table 6), and 104.8 µg/g and 341.9 µg/g (Table 7), respectively. Generally, high concentrations of Zn were observed in the livers of A. thalassinus in both the studied areas. The mean concentrations of Zn in the muscle tissues of P. anea and A. thalassinus collected from Kapar were around 26.3 µg/g and 51.0 µg/g, respectively. However, in Mersing the respective concentrations were 18.1 µg/g and 25.4 µg/g. Higher Zn concentrations were found in Kapar than in Mersing.

The observed differences can be explained by the fact that the concentrations of these metals depend to a great extent on species, sex, biological cycle, and on the part of the fish analyzed [23]. Moreover, ecological factors such as season, location/environment of development, nutrient availability, and temperature and salinity of the water, may contribute to variations in the metal concentrations in fishes. Ranges of Zn concentrations reported earlier in the muscles and livers of Malaysian marine fish were 15.4–60.1 µg/g and 27.1–95.3 µg/g, respectively [40]. Another study conducted in Langkawi Island showed that all species had higher concentrations of Zn than of other metals and that the concentrations in muscles ranged from 34.3 µg/g to 49.4 µg/g [50]. Accordingly, the Zn concentrations in the fish muscles detected by the present study are similar to those reported by [50].

In this study, the concentrations of aluminium were the highest in the gills and it ranged from 13.7 µg/g in P. anea to 538.6 µg/g in A. thalassinus in Kapar, and from 91.0 µg/g in P. anea to 850.14 µg/g in A. thalassinus at Mersing, whereas in A. thalassinus, the Al concentration was 7.2 µg/g in muscle and 28.4 µg/g in liver at Kapar station and it was 5.4 µg/g and 10.0 µg/g in the fish muscle and liver tissues, respectively, at Mersing station.

On the other hand, the concentrations of Al in the muscle and liver tissues of P. anea was 3.0 µg/g and 13.7 µg/g, respectively, in Kapar while the respective concentrations in Mersing were 1.5 µg/g and 5.1 µg/g, respectively. The mean Al concentrations were higher in the three organs fish species captured from Kapar than its concentration in the same organs of the fish species collected from Mersing except gills of A. thalassinus from Mersing. The Al concentrations were reported to fall within the range 1.50–4.50 µg/g in fish muscles from the Parangipettai Coast, India [49]. On the other hand, the Al concentrations were reported earlier to fall in the range of 31.9–166.3 µg/g in muscles and in the range of 229.01–1412.7 µg/g in gills of Malaysian marine fish from Kapar [51]. As such, the Al concentrations observed in this study generally correspond with the values reported in the literature.

Arsenic levels in the muscles of the analyzed fish ranged from 3.8 µg/g in P. anea in Kapar to 14.2 µg/g in A. thalassinus in Mersing. Whereas, the arsenic levels in fish livers ranged from 11.8 µg/g in P. anea from Kapar to 21.9 µg/g in A. thalassinus from Mersing. The arsenic levels in the fish gills ranged from 4.9 µg/g in P. anea from Mersing to 13.6 µg/g in A. thalassinus from Kapar (Tables 6 and 7). Unfortunately we do not have sufficient data of arsenic levels in fish tissues from Malaysia, to be compared with our findings.

Table 7: Concentration (µg g⁻¹ dry wt) of heavy metals (mean ± SD) in different organs of fish collected from the Mersing coastal waters, Johor Bahru, Malaysia.

<table>
<thead>
<tr>
<th>Species</th>
<th>Organ</th>
<th>Al</th>
<th>Fe</th>
<th>Zn</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. thalassinus</td>
<td>Muscle</td>
<td>5.44 ± 1.25</td>
<td>34.91 ± 1.74</td>
<td>25.39 ± 0.71</td>
<td>14.2 ± 2.34</td>
<td>0.02 ± 0.03</td>
<td>0.2 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Liver</td>
<td>10.05 ± 1.7</td>
<td>924.6 ± 24.7</td>
<td>341.9 ± 3.35</td>
<td>21.89 ± 0.9</td>
<td>2.075 ± 0.1</td>
<td>0.87 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Gills</td>
<td>850.1 ± 7.1</td>
<td>822.76 ± 9.9</td>
<td>246.55 ± 7.4</td>
<td>7.65 ± 0.1</td>
<td>0.02 ± 0.01</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>P. anea</td>
<td>Muscle</td>
<td>1.46 ± 13</td>
<td>21.47 ± 1.86</td>
<td>18.1 ± 0.79</td>
<td>3.76 ± 0.2</td>
<td>0.023 ± 0.02</td>
<td>0.17 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Liver</td>
<td>5.13 ± 0.65</td>
<td>525.96 ± 17</td>
<td>104.84 ± 1.23</td>
<td>8.38 ± 0.22</td>
<td>2.46 ± 0.02</td>
<td>1.07 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Gills</td>
<td>91.03 ± 2.7</td>
<td>461.4 ± 8.6</td>
<td>66.24 ± 1.3</td>
<td>4.88 ± 0.13</td>
<td>0.05 ± 0.1</td>
<td>1.96 ± 0.16</td>
</tr>
<tr>
<td>WHO*</td>
<td>—</td>
<td>50</td>
<td></td>
<td>150</td>
<td>0.02</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>FAO**</td>
<td>—</td>
<td>—</td>
<td></td>
<td>30–100</td>
<td>7.88*</td>
<td>0.2</td>
<td>0.5–0.6</td>
</tr>
<tr>
<td>MFR***</td>
<td>—</td>
<td>—</td>
<td></td>
<td>100</td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

According to published literature, ranges of arsenic concentrations reported earlier in the muscles of Malaysian marine fish were 1.05–2.14 µg/g [52]. Another study conducted showed that arsenic content of fish from Indian coastal waters was within the range of 0.01–0.63 µg/g [53] which are well below the arsenic levels detected in fish tissues by this study.

In this study, the lead concentrations in muscles ranged from 0.1 µg/g in *P. anea* in Kapar to 0.2 µg/g in *A. thalassinus* in Mersing. While in the livers the concentrations ranged from 1.1 µg/g in *P. anea* from Mersing to 1.5 µg/g in *A. thalassinus* in Kapar. On the other hand, the concentration ranged in gills from 1.96 µg/g in *P. anea* in Mersing to 2.03 µg/g in *A. thalassinus* in Kapar. Lead levels reported earlier in the literature fall in the range of 0.018–0.023 µg/g for muscles and 0.115–0.380 µg/g for livers of fish from Mersing. Moreover, the lead level ranged from 0.026–0.72 µg/g in muscles and 0.041–0.872 µg/g in livers of fishes from Langkawi coastal waters of Malaysia [40]. Hence, the Pb concentrations reported herein comply with these ranges.

The results of this investigation reveal that there is no significant variation in Cd levels (*P* > 0.05). The highest concentrations were observed in the livers of the fish species from Mersing, where the mean Cd concentration ranged from 2.075 µg/g in livers of *A. thalassinus* to 2.458 µg/g in livers of *P. anea* from Mersing coastal water. While the highest levels of Cd in the muscles were recorded as 0.088 µg/g in *A. thalassinus* from Kapar, in contrast, the lowest value of Cd detected was 0.021 µg/g in the muscles of *P. anea* from Mersing, whereas the Cd levels reported in the literature
fall in the range of 0.14–0.57 mg/kg and 0.15–0.52 mg/kg for muscles of _A. thalassinus_ and _P. anea_ from the same study area Kapar [51]. Another study was conducted on commercial marine fish from Klang Valley, Malaysia, which concluded that the mean Cd concentrations in the fish muscles ranged from 0.121 mg/kg to 1.594 mg/kg [54]. The third study investigated the marine fin fish captured from the coast of Langkawi Island in Malaysia and reported that the mean Cd concentrations in the fish muscles ranged from 0.30 µg/g to 0.90 µg/g [50]. Compared with the literature from different Malaysian marine coastal waters, our results for Cd concentration is lower than the literature. Cd and Pb have higher tendencies to bioaccumulate in the fish liver tissues which involves in the detoxification process. The presence of free protein-thiol group content and metallothioneins binding proteins in the liver forms a strong fixation with the heavy metals [55]. Meanwhile fish liver acts as major site for homeostasis [56].

The variability in heavy metal levels in different species depends on feeding habits [26], ecological needs, and metabolism [30], age, size, and length of the fish [57], and fish habitat [21]. Concentrations of trace metals detected in the muscle, gill, and liver samples indicate different bioaccumulation potentials. Muscles seem to be a transitory tissue in the pathway of metal uptake and in metal storage, whereas the liver appears to be the tissue, specialized in metal storage, and early uptake site of the soluble, waterborne metals in detoxification [58]. The gills comprise the chief exposure tissue and early uptake site of the soluble, waterborne metals in which metal concentrations are the highest in the early stages of exposure, before these metals are transported to other fish tissues [59]. Although human activity is concentrated in the west coast of Peninsular Malaysia, compared with the east coast, there is some contamination with heavy metals in the east coast. The results of the present study suggest that, at some point, sources of heavy metal contaminations are present in the east coast of Peninsular Malaysia in spite of the relatively low human activities.

The relationships between body size and trace element concentrations in the two fish species were also investigated and significant positive correlations between the total fish length and weight and heavy metal concentrations were found (_P. anea_ had higher Zn concentration, and the gills of _A. thalassinus_ from both Kapar and Mersing had higher Al and Zn levels, respectively. Moreover, the _A. thalassinus_ species had higher metal concentrations than the _P. anea_. In water samples, Cd concentrations in both sites exceed the international standards, but still in the permissible levels of national standards. The mean concentrations of heavy metals, analyzed in the muscles of both species, were lower than the maximum concentrations recommended by [61–63]. The concentrations of Al, Fe, Zn, As, Cd, and Pb in muscle tissues should pose no acute toxicological risks to human health. This study revealed that the studied metals contaminations are generally low in the tissues of the examined fish in the two study areas. Although the levels of these heavy metals are not high, a potential danger may emerge in the future depending on pollution sources. The data may be taken as a convenient base line against which any future pollution trends can be evaluated.

### Abbreviations

- cm: Centimeter
- g: Gram
- µg/g: Micrograms per gram
- µg/L: Micrograms per liter
- Mg/L: Milligrams per liter
- SD: Standard deviation
- RSD: Relative standard deviation.

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### References


Research Article

Involuntary and Persistent Environmental Noise Influences Health and Hearing in Beirut, Lebanon

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Objective. This study was conducted to assess the effects of involuntary and persistent noise exposure on health and hearing among Lebanese adults in Beirut, Lebanon, where people are exposed to noise from construction sites, power generators, honking cars, and motorcycles.

Methods. Using a descriptive and exploratory design with mixed methods, participants were surveyed, interviewed, and tested for hearing while street noise levels were measured near their residents and work places.

Results. Self-reports of 83 Lebanese adult, who lived and worked in Beirut, helped identify common patterns in experiences such as irritability, anger, headaches, and sleep disturbances due to noise annoyance. Of those tested, 30% suffered from high-frequency hearing impairment. Our results showed that environmental sound dB had increased by 12% and sound intensity by 400% above the maximum standard level when compared to the WHO report of 1999.

Conclusion. Environmental noise contributes to premature hearing loss and potentiates systemic diseases among Lebanese.

1. Introduction

The unrecognized effects of persistent exposure to environmental noise on health and hearing and the unexplored nonspecific responses to noise pollution in Beirut, Lebanon, were the focus of this study. Literature [1] reports have identified excessive external noise and smoking as a major cause of hearing loss and impairment among children and young adults. The nonmodifiable contributing risk factors are listed as age, genetic trends, male gender, and race. Modifiable factors are voluntary exposure to loud music, smoking, sports, diet, dental hygiene, and systemic diseases [1, 2].

The city of Beirut is a metropolitan and multicultural venue with high-rise buildings erected to replace traditional one-family dwelling and occupy a vast portion of the Mediterranean shores in condensed populated areas. The environmental noise associated with ongoing power generators and construction sites begins at dawn and continues through the night as honking cars and motorcycles zigzag through crowded narrow streets. There is no escape from noise since commercial and residential zones are adjacent in close proximity where people live above the shops and businesses. Incessant honking is an expression of frustration when narrow streets are blocked by parked cars on both sides and fruit vendors at each intersection.

In a surveyed community response to noise in Beirut, Lebanon [2], participants identified the main sources as motorcycles (70.4%), traffic (63.1%), and car horns (56.3%). Reported construction and generator annoyance were 42% and 55.1%, respectively. This study aims to identify the current level of persistent environmental noise effect on hearing and overall health among Lebanese living and working on Hamra in Beirut, Lebanon.

In a study of 440 local residents of Beirut, ages 21–50, researchers examined the effects of environmental noise and smoking on hearing loss [2]. They divided the participants...
into 4 groups of smokers and nonsmokers living in noisy (70–90 dBA) and quiet areas (45–55 dBA) and found hearing loss among the smokers when exposed to 8000 Hz at high frequencies and more hearing impairment among smokers above age 40+. Younger nonsmokers (21–39) showed significant hearing impairment at low frequencies.

Environmental noise and health were found [3] closely related when researchers assesses 105 adults living near Auckland International Airport in New Zealand for noise sensitivity and annoyance for any adverse health effects. They identified that noise contributed to sleep disturbance and reduced health-related quality of life. Similarly, 2,312 people living near Frankfurt Airport [4] were given environmental (EQoL) and health-related (HQoL) quality of life instruments to assess their experiences with aircraft noise annoyance and disturbances to their life quality. Researchers compared their findings from aircraft noise with exposure to road traffic and railway noise, and results suggested a recursive relationship between noise and health.

Numerous empirical studies have identified long-term exposure to noise as a major health concern. Noise from siren or ambulance can generate an immediate protective reaction known as fight or flight. In a substantial review [5] traffic noise effects were found as a source of environmental annoyance. Referencing the Environmental Expert Council (EEC) of Germany, noise was reported as a major source of severe annoyance and distress. The fastest and most urgent signal to noise is mediated by a subcortical area on amygdala. Even during sleep, the environmental noise from airplanes or heavy equipments can generate dangerous brain signals to release stress hormones. The chronic release of stress hormone from long-term exposure to environmental noise increases the endogenous risk factors such as ischemic heart disease and myocardial infarction [5]. Because each individual study on the adverse health effects of noise in most cases does not reach statistical significance, meta-analysis of multiple studies [5] according to EEC shows a consistent trend towards cardiovascular risk when daytime noise level exceeds 65 dB(A). However, the urgent call for public health safety to reduce extra-aural occupational noise remains misclassified and warnings ignored.

Unprotected and regular exposure to occupational loud noise in the daytime interferes with nocturnal sleep patterns. Researchers [6] divided 3 groups of 8 subjects (n = 24) and exposed them to continuous noise at >75 dB for 1–2 years, 5–10 years, and over 15 years and matched them with corresponding healthy control groups who worked in a quiet environment. After using PolySomnoGraphy (PSG) for an all-night sleep study, subjects rated their sleep quality on a Visual Analogue Scale (VAS), and the results showed that workers who were exposed to occupational noise had poor quality sleep and over the years adapted to noise. However, the long-term adverse health effects of noise hidden in an adaptive process or subsequent systemic diseases were not investigated. Assessing the sleep quality of air travelers and their exhaustion level after sleeping on flights may better reveal brain responses to unrecognized and constant noise.

According to the 1998 WHO report [7], Lebanon occupies 10, 452 square kilometers (Km²) of land strip with a population of 4.5 million residents. Over 80% of Lebanese reside in crowded urban areas in high-rise buildings. Researchers [8] have examined the quality of life in high-rise buildings or controlled built environments (CBE) and found them incompatible with the psychological needs of women and children. The recent social architects place multiple families in one high-rise building, and residents exposed to overcrowding, external loud noise from proximate airports or railroads, air pollution, toxins, and malodorous sewer are those experiencing nonspecific stress manifested as irritability and aggression similar to patients in hospitals and convalescent centers or air travelers kept in CBEs such as airports who experience stress.

Farmers using farming equipment are at risk for noise-induced hearing loss [9]. Ninety three industrial farmers between the ages of 18–75 were surveyed after complete health history and demographic data on noise exposure. Their bilateral hearing sensitivity was assessed, using air conduction audiometric testing at 500–800 Hz frequencies. Farmers compared their findings from aircraft noise with exposure to road traffic and railway noise, and results suggested a recursive relationship between noise and health.

Noise at a certain frequency and decibel is detrimental to hearing and according to the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) (see Table 2) outdoor exposure to the environmental noise should remain within an acceptable range to avoid hearing loss [10–13]. According to the WHO report published by the Lebanese Ministry of Environment, the noise level in Beirut, Lebanon could have adverse health effects on the local residents (see Table 3). The physiological effects of environmental noise have been associated with the endocrine changes [14, 15].

2. Methodology

The purpose of this study was to examine the local perceptions on environmental noise levels and how exposure to involuntary and persistent noise affected young Lebanese health and hearing. To assess street noise level and its health and hearing effects, a cross-sectional design was adopted using mixed methods and the critical theory of participatory action according to Freire [16]. This exploratory and descriptive investigation was focused on individual experiences with persistent noise.

Assured of anonymity and confidentiality participants willingly engaged in informal dialogues and interviews for 30–60 minutes. Interviews took place at various locations including workplace, shops, dormitories, or outdoors. Interviewers helped participants recall and explain past and present experiences with noise at different peak hours and
Table 1: Physiological and psychological effects of noise pollution.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annoyance</td>
<td>Even relatively low levels of noise can cause annoyance and frustration. A tranquil background can make noise more intrusive. Natural sounds are generally less annoying than unnecessary or controllable sound such as car horns. For instance, intermittent sounds such as a tap dripping on a quiet night can be more disturbing than the sound of falling rain.</td>
</tr>
<tr>
<td>Speech interference</td>
<td>Noise can interfere with speech. When the background noise level is 50 dBA, normal conversation can be easily carried with someone up to 1 m away. Any more than that, problems will arise.</td>
</tr>
<tr>
<td>Sleep interference</td>
<td>Noise can wake people from sleep and keep them awake. Even if not actually woken, a person’s sleep pattern can be disturbed, resulting in a reduced feeling of well-being the next day. External noise measuring up to 30 dBA in a bedroom is appropriate for sleep.</td>
</tr>
<tr>
<td>Decreased work performance</td>
<td>Noise pollution can make people nervous. Accordingly, it can prevent people from concentrating on their work. As noise levels increase, ability to concentrate and work efficiently and accurately reduces. Louder noise bursts can be more disruptive. Noise is more likely to reduce the accuracy of the work than reduce the total quantity of work done. Complex tasks are more likely to be impaired.</td>
</tr>
<tr>
<td>Hearing loss</td>
<td>Prolonged exposure to noise levels above 85 dBA can damage inner ear cells and lead to hearing loss. At first, hearing loss is usually temporary and recovery takes place over a few days. After further exposure, people may not fully recover and develop deafness. The extent of deafness depends on the degree of exposure and individual susceptibility. Even brief exposure to very high levels of 130 dBA or more can cause instant, irreversible hearing damage. Research has shown that noise is one of the leading causes of hearing loss for millions of people with impaired hearing in the United States.</td>
</tr>
<tr>
<td>Physiological changes</td>
<td>Noise can change a man’s physiological state by speeding up pulse and respiratory rates. There is medical evidence that noise can cause heart attacks in individuals with existing cardiac injury and that continued exposure to loud noises could cause such chronic effects as hypertension or ulcers. According to medical studies, there is an increased risk to the cardiovascular system from a sound pressure level of above 65 dBA.</td>
</tr>
</tbody>
</table>

References [12–15]

Table 2: Brief USEPA and WHO recommended sound levels for community noise.

<table>
<thead>
<tr>
<th>Level</th>
<th>Effect</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>USEPA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L&lt;sub&gt;eq&lt;/sub&gt; (24) &lt; 70 dB&lt;sup&gt;*&lt;/sup&gt;</td>
<td>Hearing outdoor activity</td>
<td>All outdoor areas including residential zones, farms, and other places where people spend varying amount of time and places in which quiet is the basis for use.</td>
</tr>
<tr>
<td>L&lt;sub&gt;d&lt;/sub&gt;n &lt; 55 dB&lt;sup&gt;**&lt;/sup&gt;</td>
<td>Interference and annoyance</td>
<td>Outdoor areas where people spend limited amount of time such as school yards, and playgrounds.**</td>
</tr>
<tr>
<td>L&lt;sub&gt;eq&lt;/sub&gt; (24) &lt; 55 dB</td>
<td>Outdoor activity interference and annoyance</td>
<td></td>
</tr>
<tr>
<td><strong>WHO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L&lt;sub&gt;eq&lt;/sub&gt; (24) = 55 dB</td>
<td>Serious to moderate annoyance</td>
<td>Outdoor living area</td>
</tr>
<tr>
<td>L&lt;sub&gt;eq&lt;/sub&gt; (24) = 70 dB</td>
<td>Hearing impairment</td>
<td>Industrial, commercial shopping, and traffic areas, indoors and outdoors</td>
</tr>
</tbody>
</table>

References [10–13]

<sup>*</sup> Level equivalent of sound (L<sub>eq</sub>) is the energy average noise level (usually A-weighted) integrated over some specified time. Also referred to as Equivalent sound pressure levels.

<sup>**</sup>L<sub>d</sub>n = loudness.

describe how noise influenced their lives and probed for any pattern changes in sleep quality, appetite, and unrecognized stress. This study was initiated in September 2009 and ended in May 2010. Written consent in English and Arabic emphasized no risk for voluntary participation. Basic human rights to freedom were closely observed, and participants were given an opportunity to withdraw from the study at any time.

2.1. Data collection. A multidisciplinary research team of nursing, medicine, and engineering with cultural literacy retrieved ethnographic data according to Spradley [17]. Standard demographic survey questionnaire obtained personal data on education, employment, income, and interviews using open-ended questions focused on past and present health and hearing status and personal approach to stress management. Verbal description and self-report
offered valuable personal experiences and concurrently were compared with literature. Recorded and expanded data reached saturation upon two rounds of transcription and were analyzed. Further networking with participants provided sufficient opportunities for clarification. Data were safely stored for future reference.

The initial proposal was aimed to include 100 equally divided men and women, and after randomly approaching residents and shop keepers on Hamra Streets we could only recruit 83 volunteer adult Lebanese (46 men and 37 women). Researcher and two graduate assistants from nursing administered survey questionnaire and interviewed participants for personal experiences with noise. One research assistant from engineering measured street noise levels in areas where participants worked and lived. Research team worked in rotations and frequently compared data to match participants with locations for increased data accuracy. Informal and semi-structured interviews using open-ended questions helped retrieve participants’ experiences and perceptions with noise to identify their ways of coping or adjusting to environmental noise. Participants were offered a small incentive to compensate for their time and cooperation. Anonymity was assured, and raw data was secured in locked office cabinets.

Demographic data provided age range, the number of years working and/or living on premises, income, and education level. Interviews helped obtain information on health habits such as diet, sleep, and coping techniques. Later, participants were tested for hearing using pure tone screening to determine hearing impairment or loss. The street noise levels were measured at 4 busy intersections near participants’ home and workplace using sound level meter (SLM).

Our inclusion criteria consisted of Lebanese men and women between the ages 18–38 who lived and worked on Hamra Street for longer than 6 months. We chose a younger age group to eliminate age-related hearing loss or impairment and health complications associated with advanced age. Because this study was conducted in a metropolitan area and the majority of people in Beirut are trilingual (Arabic, English, and French) we chose to include people with basic language literacy (read and write) and unexposed to voluntary noise such as loud music.

2.2. Findings/Results. Data were analyzed through an immediate debriefing after each interview and compared with field notes and visual clues. Data was reviewed line by line and coded using the four phases of qualitative study by Polit and Hungler [18]. Author’s personal experiences with noise annoyance verified published literature to substantiate scientific adequacy and data credibility. Verified data were compiled upon saturation and analysis. The inquiry audit and neutrality were established for dependability and data conformity. Transferability of the framework was unanimous among scholarly colleagues and their personal reflections on noise annoyance.

Researcher and two assistants randomly approached people at various shops, stores, apartment buildings, and dormitories on Hamra Street where residents and shopkeepers often gathered to visit. Consenting participants were later met at a location of their choosing to be surveyed and interviewed. On the same day an appointment was made for each participant to meet individually or as a group for hearing test at the audiology clinic. In three occasions when 4–5 participants were waiting for hearing test, focus group discussion was held ranging from 60–90 minutes to explore more experiences with noise. At other occasions interviews were held at the store, at home, in dormitory, or outdoors.

Standard demographic data revealed an average age of 26.5 for men and 27.3 for women, with mixed educational, income, and employment backgrounds. At interviews participants were asked to elaborate on their daily experiences with environmental noise, and 70% (58) had difficulty sleeping at night, and according to the noise meter results they were exposed to Leq 12 hr >50 dBA. In support of our findings multiple studies [7, 19, 20] have reporting the degree of annoyance, sleep disturbance, and hearing loss related to traffic noise in residential urban communities. Using a questionnaire on the influence of environmental noise on health, researchers [19] sampled 1000 individuals ages 19–80 in a heavy traffic area in Stockholm and found frequent annoyance among 13% of subjects exposed to Leq 24 hr >50 dBA when compared to the 2% who were exposed to <50 dBA. Sleep disturbance were reported by 23% at Leq 24 hr >50 dBA and by 13% exposed to <50 dBA. Habituation to noise has been more related to sleep rather than annoyance. Annoyance and sleep problems were prevalent among those with bedroom windows facing the streets or living in apartments [21].

Most studies on noise report human responses, and few have explored coping with constant noise. Our study focused on finding various forms of coping skills when participants shared experiences with increased craving for sweets 55% (45), caffeine intake 62% (51), and smoking 78% (65). More women 81% (30) in the study reported frustration, anger, and feeling helpless as an aftereffect of persistent noise. Men 93% (43) revealed habituation to noise by unrecognized and later described techniques such as chewing gums or tooth picks, snacking at work, and managing to sleep at night by
using other incessant noise such as bathroom fan, radio, and television. Afternoon headaches were common among women 78% (29). The unexpected fear of knowing about hearing status 96% (80) among men and women revealed that majority of participants had suspected some hearing impairment when family members complained about having to speak louder or repeat themselves.

Literature support identifies imbalance in endocrine system linked to emotional disturbance. Researchers [21, 22] remain uncertain about the habituation to stress and posit that repeated exposure to external stimuli can shape adaptive brain plasticity mechanism in response to homotypic challenges when cortical auditory processing areas respond to repeated loud noise.

Study limitations were few including low budget funding, time line for project completion per 10 months Fulbright contract, long delays for obtaining IRB approval to proceed with data collection, and participants who were business owner and could not leave their work to be tested for hearing or feared results.

Participants experienced the physical and emotional effects of persistent noise in form of irritability, anger, nausea, headache, and sleep disturbances. Men 93% (43) mainly reported nervous eating, chewing (gum or tooth picks), and both genders 78% (65) smoked to relieve agitating discomforts (described as auditory disturbance on an aircraft). Participants showed concerns for recent weight gain 51% (42), hypertension 46% (38), and diabetes 54% (45). We assessed participant’s hearing, and our measurable indicators and output activities were achieved using audiometer pure tone testing. We found bilateral hearing sensitivity upon assessment by air-conduction audiometric testing at 500–4000 Hz frequencies. Of those tested 40% (33), there were 30% (10) who suffered from asymmetrical high-frequency hearing loss and impairment.

Street noise levels were measured by sound level meter (SLM) near participant’s home and workplace at 4 intersections on Hamra and Bliss streets. We selected similar time frames and durations to match the WHO study of 1999 for increased accuracy in comparison. Tabulated and analyzed data showed an increase in environmental noise level between 1999 and 2009. The mean average noise standard dBA by the WHO report during 7 am to 6 pm was 55–65, and in 2010 it was 65–75 with a 12% increase in sound dB and 400% increase in noise intensity (Tables 4 and 5).

### 3. Discussion

As discovered, Lebanese cope with persistent noise in various forms such as smoking, consuming strong coffee, and sweets. To describe caffeine effects on stress response associated with noise, researchers [22] have reported that high doses of caffeine, a psychoactive substance, can activate hypothalamus-pituitary-adrenal axis (HPA), and low doses of caffeine can restrict some of the stress responses by HPA axis. Also, elevated stress due to loud noise was assessed [23] to find how noise influenced adrenocorticotropic hormone (ACTH) and corticosterone levels in animals with and without caffeine intake. Plasma ACTH and corticosterone levels peaked 30 minutes after exposure to noise and rapidly declined when noise was eliminated. Then low-dose caffeine at 2 mg/kg was injected to find a significant increase in plasma corticosterone and ACTH levels within 30 minutes and return to baseline after 60 minutes. When higher doses of caffeine (30 mg/kg and higher) were injected, the hormone levels increased and lasted for at least 2 hours in response to loud noise.

In this study participants experienced various noise-related physical responses. Researchers [6, 22, 23] showed perceived threat from loud noise on HPA axis and the release of ACTH as corticosterone. Exposure to noise at night in acoustic chambers using various intensities showed elevated plasma ACTH and corticosterone at 85 dB. Many regions of the brain showed negative response to noise due to audiogenic stress which provoked HPA axis with life-threatening responses.

We found participants expressing rage and frustration by honking and shouting when they could not control noise exposure. Similarly, an investigation [24] of 10 healthy human volunteers who were exposed to loud noise at 100 dB under controllable and uncontrollable conditions on two separate days revealed noteworthy results. Participants self-rated their responses, and both groups reported a higher sense of helplessness, lack of control, tension, stress, unhappiness, anxiety, and depression. There was a greater HPA axis response higher plasma adrenocorticotropin hormone levels and increased levels of sympathetic nervous system electrodermal activity among those exposed to uncontrollable noise [22–24]. Therefore, losing control over aversive stimulus can negatively affect mood and overall health.
This study with literature support highlights many aspects of noise influence on health. The long-term exposure to the environmental noise can pose a threat to health by triggering responses from neuroendocrine and autonomic nervous system.

4. Conclusion

In a nonspecific and unrecognized way, noise can generate an unsettling level of stress with profound influence on general health. Upon our initial approach, Lebanese seemed fully aware and yet resigned toward noise problem. Common thread for adaptation to noise in this study was reported as a series of unhealthy habits and public expression of anger and rage by shouting and honking. Noise and uninvited sounds [25] adversely influence physical and psychological health. Lebanese men and women exposed to chronic noise and tested showed hearing loss at high frequency range, and those who could not attend testing sessions due to long work hours expressed fear of hearing impairment according to family members’ complaints for having to speak louder or repeat themselves.

In the United States, nearly 10 million adults and 5.2 million children suffer from irreversible noise-related hearing impairment, and 30 millions are at risk for daily exposure to dangerous levels of noise. The noise-related health effects are often ignored and yet significant such as hypertension, tachycardia and elevated cortisol levels, and stress [9, 12, 24].

Finally, our results showed that environmental sound dB had increased by 12% and sound intensity by 400% above the maximum standard level when compared to the WHO report of 1999 which confirms noise as an increasingly recognized global problem with consequential effects on life quality. This study was an attempt to bring awareness to how noise could affect hearing and over time influence daily behavior leading to systemic diseases. Although this study included seemingly healthy young adults (ages 18–38), we still found them at risk for non-age-related hearing loss. Potential for temporary or permanent loss of hearing among children and young adults warrants greater focus on public education and awareness on noise hazards.

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