Multivariate Benchmark Dose Method for Monitoring Groundwater Quality

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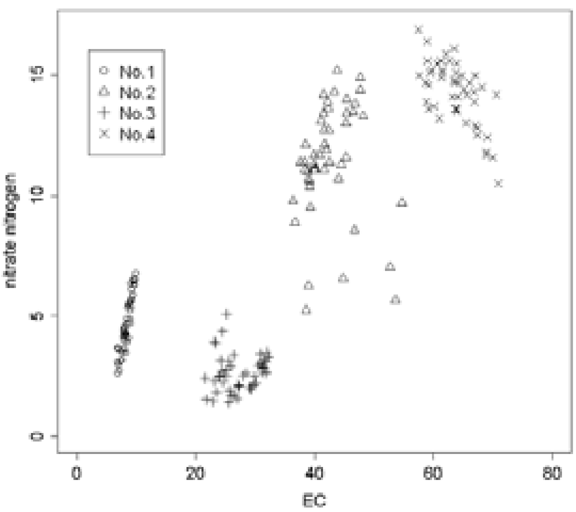
Introduction

Sewage sludge is the residual material resulting from the treatment process of residential and industrial waste. Before a 1987 ban, sludge was often dumped into the ocean. More recently sewage sludge has been used as a compost. Unfortunately the composting of this sludge is not without hazards. Sewage sludge can contain heavy metals such as cadmium, lead, arsenic and mercury; disease-causing organisms such as bacteria, viruses and parasites; and toxic organics such as PCB.s and pesticides. (Hope 1986) Even as incineration has increased, adequate disposal techniques are still required for the contaminated ash. (Werle et al. 2010). Groundwater contamination, caused by low quality processing of sewage sludge and incinerated ash, is regarded as a serious problem demanding a cost effective method for its monitoring (Tredoux et al. 2004). Recently a number of reports have proposed Electrical Conductivity (EC) or Chloride (Cl) as effective parameters to monitor pollutants (Kney et al. 2007). Few however, have clearly determined the allowable limit of the EC or Cl values for groundwater polluted by sewage sludge leachate or incinerated ash. In this study, we use the “benchmark dose” (BMD) approach (Crump 1984), which was originally developed to determine the allowable limit of exposure to such contaminants as dioxin, Cd, and Hg to obtain a local allowable limit of EC and Cl for the monitoring of groundwater quality.

Background and Data

Environmental standards, or allowable limits, of water quality are necessary for effective monitoring of groundwater quality by civil services (Shober et al. 2003). An environmental standard is a threshold value, set as a result of risk assessment of reliable data and made with sound scientific knowledge for the management of human health for potentially harmful agents. The major obstacle to establishing the allowable limits of water quality tests is that the quality of groundwater differs considerably from one site to another. Some of the factors excluding contamination affecting groundwater quality are soil composition and groundwater sources. To take into account the natural background conditions, it is normally required to include a non-contaminated control site for monitoring (Kney et al. 2007). This is based on the idea that any human origin contamination may be detected by comparing it with a natural control site. It is essential that both sites be as similar as possible in order to detect human activity contamination.

Among a number of water quality tests available, electric conductivity (EC) and Chloride (Cl) are the most widely used for monitoring waste repositories. In Japan either or both of them, depending on the situation, are required for tests conducted at final disposal sites. This study focuses on establishing allowable limits for EC and Cl for use as effective monitors of groundwater contamination.



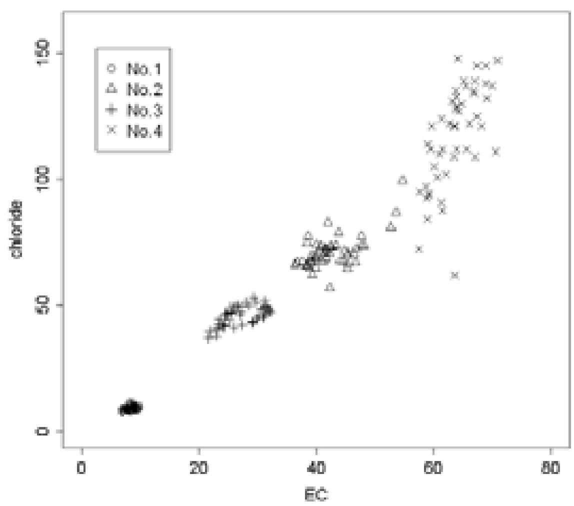


Figure 1. *Scatter* plot of NO_3-N and EC (left) and that of EC and Cl (right) at the boring sites.

The study area is “Sanpou” Mountain located just east of Nagasaki city. There is a final disposal plant atop the mountain, a few homes about 300m below and a water reservoir a further 3km below that which provides drinking water to 40% of the citizens of Nagasaki. The plant started operation in 1975 and had dumped and buried sewage sludge, incinerated ash and industrial waste on and into the surrounding land heedless of any established standards or regulations, before a law prohibiting this dumping was enforced. The accumulation of this waste has now polluted groundwater flowing under the plant.

In 1997, water quality test data was falsified by the Nagasaki City Hall, and some citizens filed a criminal complaint with Nagasaki City and the plant for possible illegal disposal techniques. This affair prompted Nagasaki City Hall to perform a comprehensive survey of soil and groundwater contamination around the repository site in 1998 and detailed groundwater monitoring has been performed regularly since then. This study is concerned with four boring sites. Figure 1 (left) shows the relationships between EC and NO_3-N in the four sites. Site No.1 is in a national forest where human activity is prohibited and more importantly not in the same aquifer as the treatment plant. The pristine region site No.1 was set as the natural control. Sites No.2 and No.4 were confirmed to be contaminated by sewage sludge with 86% and 100% of NO_3-N measurements exceeding the standard value 10 mg/l. On the other hand, site No. 3 was high in Cl but low in NO_3-N, which is typical of incinerated ash leachate. Figure 1 (right) shows that EC and Cl are clearly linearly related if the four sites are combined. This finding is commonly observed in contaminated sites (Liu et al. 2003). Intrasite relationships between EC and Cl, however, are not very clear.

Relationships between EC and NO_3-N vary widely among our sites (Figure 1 left). In general there is a considerable range in values for even basic water quality tests for monitoring sewage sludge leachate (Wilson et al. 1996). This fact stands as an obstacle to establishing the allowable limit of water quality tests.

BMD

Allowable limit for the daily intake of dioxin was determined based on the benchmark dose (BMD) method originally suggested by Crump (1984). Various organizations and regulatory agencies in the US and abroad have considered adoption of its use (US EPA 2007). The BMD approach has been considered in the international arena as part of the effort to develop a standard approach (Murrel et al. 1998; Rice 2004). Briefly, the BMD is defined as the lower 95% confidence bound on dose which results in some pre-specified acceptable level of risk. BMD is particularly useful when observed dose-response relationships are reliable but do not contain the pre-specified level of the response. As for the dioxin case, experiments were performed with extremely high doses to observe sufficiently large number of responses, in this case hepatic cancer, for reliable statistical analysis, and then the dose-response curves were extrapolated to a range including the pre-specified level of risk taking into account the uncertainty involved in the statistical analysis.

Applying the BMD approach to groundwater monitoring has some peculiar aspects as compared to the above toxicological applications. Originally, BMD method was developed targeting a binary endpoint, or whether an event of interest is observed or not, such as a cancer or a malformation. For instance, Portier (2000) uses a 1% increase of the event over non-exposed controls as an acceptable limit. Murrell et al. (1998) define a modified BMD for making comparisons among various endpoints more meaningful. Sand et al. (2007) illustrate epidemiological applications with a continuous response variable.

When developing water quality standards, the latter approach seems appropriate, since water quality test results are normally continuous measurements. Also in the toxicological application, the value of a response variable is assumed to be determined by the value of an explanatory variable by a well-controlled experimental design. The results are usually described as a dose-response curve in a two-dimensional scatter plot. In the groundwater monitoring however, the value of a response variable usually depends on a number of environmental and contaminating factors. Therefore, it is interesting to explore a multivariate analogue of the original BMD approach for an effective monitoring method.

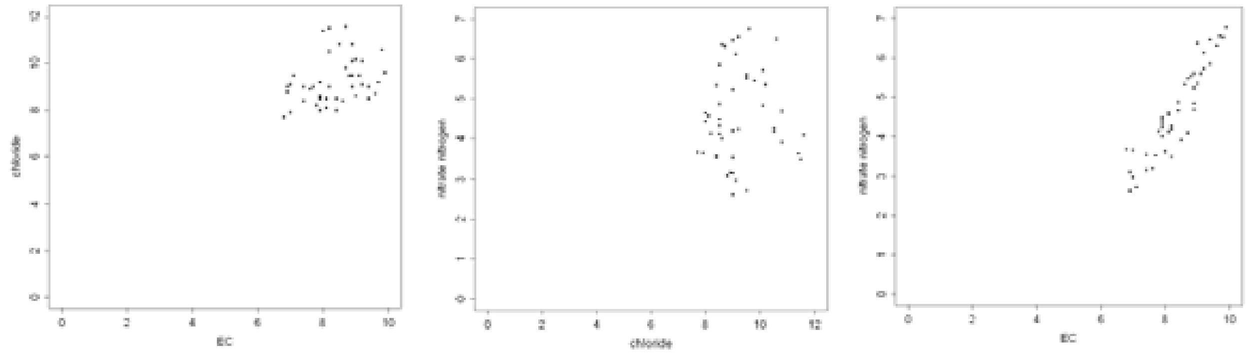


Figure 2. Scatter plots between EC and Cl (left), Cl and NO_3-N (center) and EC and NO_3-N (right) in control site No. 1

In this study, NO_3-N is treated as a response variable, since a legal limit for NO_3-N has been determined. EC and Cl are the explanatory variables, because they are closely related to NO_3-N, and are the standard markers used to monitor groundwater at final disposal sites although no legal limit for them has been determined. We use the legal limit of NO_3-N in Japan, 10mg/l, as a pre-specified acceptable limit. We will examine relationships between NO_3-N, EC and Cl under contaminated and uncontaminated environmental conditions. Then will obtain an allowable limit of a combined value of EC and Cl by applying the BMD approach. The key concept of this method is natural control water which refers to groundwater at a control site which is under the same geographic and hydrologic influences as the monitoring site but without human originating contamination.

Results

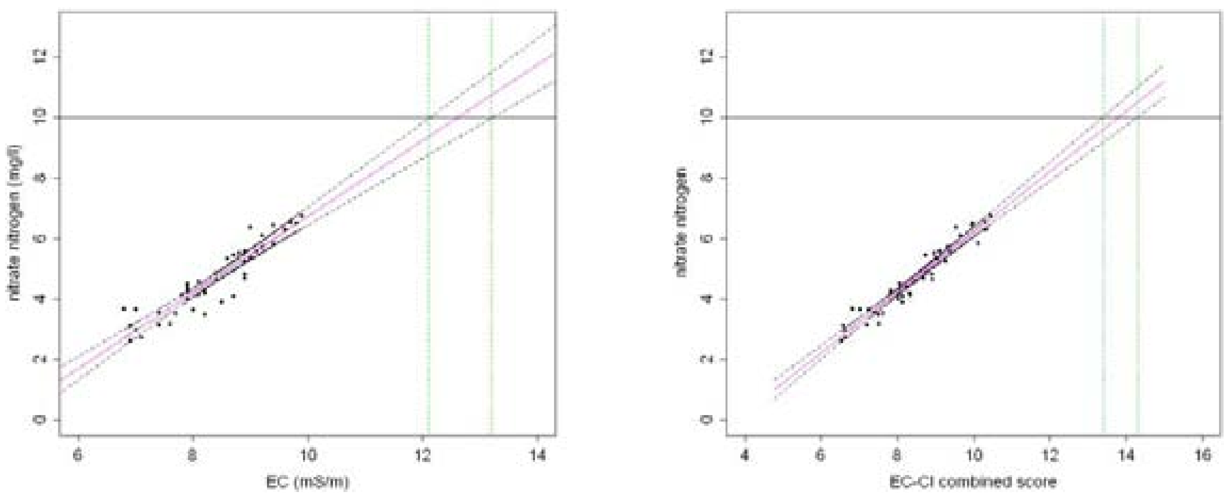


Figure 3. Scatter plot of EC vs. NO_3-N (left) and EC-Cl combined score vs. NO_3-N (right). The upper and lower 95% confidence limits are displayed.

Figure 2 presents the results of the water quality tests for site No. 1 performed four times a year between 1998~2010.This demonstrates the relationships between NO_3-N, EC and Cl under undisturbed natural conditions, where the variation in NO_3-N is possibly due to fluctuations in the amount of precipitation or fallen leaves caused by seasonal changes, unrelated to human activity. There is a strong linear relationship between EC and NO_3-N. The linear regression model was obtained as NO_3-N= -5.85 + 1.26 EC (r=0.926). This model presented lower and upper BMD values 12.1 and 13.2, respectively (Figure 3, left). In mathematical notations;

$$\Pr\{E(NO_3\text{-}N \mid EC>12.1)>10\}>0.05 \text{ and } \Pr\{E(NO_3\text{-}N \mid EC>13.2)>10\}>0.95$$

This indicates if EC> 12.1 or 13.2 is observed, then NO_3-N> 10 holds likely or almost certainly, respectively.

On the other hand, a multiple regression model with EC and Cl as explanatory variables was

$$NO_3\text{-}N=-3.77+1.37EC -0.32Cl \quad (r=0.964)$$

The equation 1.37EC -0.32Cl will be referred to as "EC-Cl combined Score" or simply the combined score. The model presented lower and upper BMD values 13.4 and 14.3, respectively (Figure 3, right). That is,

$$\Pr\{E(NO_3\text{-}N \mid Score>13.4)>10\}>0.05 \text{ and } \Pr\{E(NO_3\text{-}N \mid EC>14.3)>10\}>0.95$$

It appears from comparing the two graphs that the combined score substantially improves the model fitness over EC alone. The improvement of the fitness will also improve the validity and relevance of the allowable limits in practice. Based on the results, we propose 13.4 and 14.3 of the combined score as warning and alarm signals, respectively. In other words, the combined score>13.4 prompts an investigation into cause, and a combined score>14.3 requires detailed testing to positively identify and remove the cause.

We will give brief accounts of the logic in applying the allowable limits for monitoring. Let us denote by S the combined score. First, if we observe S>14.3 or >13.4 with groundwater in No. 1, then it is almost certain or likely, respectively, that NO_3-N > 10mg/l. Secondly, suppose we observe S>14.3 or >13.4 when monitoring groundwater in a certain site different from No. 1. This case is more interesting and needs more careful consideration. There are two possibilities; that is, whether the site is contaminated with human-origin pollutants or not. If it is polluted by human-origin contaminants, then the site should be examined with detailed water quality tests to identify and remove the cause of the pollutants. If not, then the site is equivalent to the natural control site No. 1, and therefore it is almost certain, or likely, respectively, that NO_3-N > 10mg/l. Therefore, detailed water quality tests should be performed to confirm the value of NO_3-N and examine possible causes of the large score. Thus, in either way, S>14.3 or >13.4 prompts a search for the cause or to perform a detailed examination of groundwater quality.

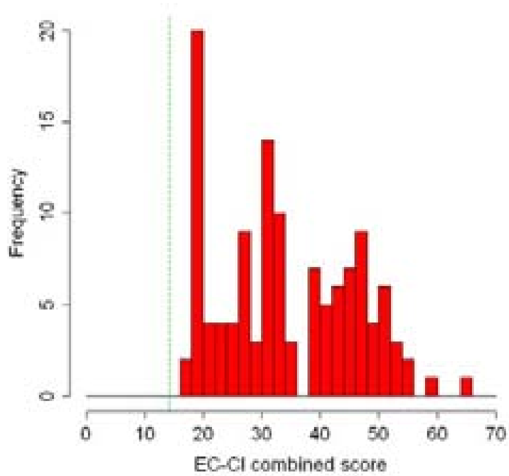


Figure 4. Histogram of the combined score for sites No. 2, 3 and 4. The vertical line denotes 14.3

To examine the performance of the allowable limits, we calculated the combined score for each of the test results shown in Figure 1 except for those concerning site No. 1. The scores are shown in Figure 4, where the dotted vertical line indicates the upper limit 14.3. All of the test results exceed the limit values.

3. Discussion

Threshold values are of prime importance in providing a sound basis for public health decisions. We were concerned how to define a logically sound limit of EC and Cl for monitoring groundwater quality in waste repositories since EC and Cl are the parameters most widely used in water quality tests and often mandatory for final disposal plant monitoring. Our conclusion is to propose a method to establish a local limit according to the peculiar nature of each site.

The most salient feature of proposing a local allowable limit is that it is determined only by the water quality of the control site. Sand et al. (2008) also set their pre-specified acceptable level of a response variable as corresponding to the 5th percentile of the control distribution. The idea has been medically practiced in determining the normal range of clinical biochemical tests. The allowable limit determined in this way is applicable to unknown contaminations we may face in the future. Another special feature of our method is that it uses the environmental standard for NO_3-N (10 mg/l) as the pre-specified acceptable level required for applying the BMD method. In this way, the allowable limit determined for EC and Cl is associated with a legal significance. The environmental standard for NO_3-N is currently set for the WHO and most countries at 11.3, and at 20 in China. In all of these countries our methods are readily applicable.

The effects of setting an environmental standard for EC and Cl as an effective measure of groundwater quality by civil services is undeniable and will greatly help in correctly identifying contaminated sites. The method we described to determine these environmental standards is expected to have an impact on the development of environmental regulations for groundwater contamination around the world.

4. References

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