Bull Environ Contam Toxicol (1984) 32:503-509

Environmental Contamination and Toxicology

A Statistical View of Heavy Metal Pollution Index of River Sediment

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How to set up a standard method for judging as to whether or not river sediment is polluted by heavy metal is essential to the definition of polluted sediments(Pilotte et al . 1978; Joung et al.1979; Landwehr 1979). In the previous report (Nishida et al.1982), we proposed a pollution index to determine the degree of pollution and how it was applied to the sediment of first class rivers in Japan. The first class rivers were designated by the Japanese government in 1963 as important in the national land conservation and economic programme.

The fundamental philosophy of this method is based on the statistical idea that the upper 10% of the distribution formed by the normalized group of upstream sediment falls within the critical region. In this case the distribution of pollution indices $\{t_i(i=1,2,...,N)\}$ must be normal, where the subscript i stands for the i-th river. If $\{t_i\}$ does not display normality, there is no other alternative but to set the point of 90% of the cumulative frequency distribution of $\{t_i\}$. Thus, as $\{t_i\}$ is not always a definite distribution, a general method for calculating the critical point of pollution is not defined.

In the present paper we propose a new pollution index, which is distributed as noncentral chi-square in most of the cases of practical application.

THEORY

Let x_{ij} denote the average of the concentration of k independent measurements on the j-th metal in the sediment of i-th upstream river. The distribution of heavy metal concentration in sediments is considered to be the logarithmic normal type. Thus, if we take the logariyhm of the concentration of each element x_{ij}, then the elements $\{\log_{10}(a+bx_{ij})\}$ for each heavy metal are considered to be a random sample of size N from a normal distribution $N(\mu_j,\sigma_j^2)$,for which the estimates of μ_j and σ_j^2 are given by the expressions (1) and (2), respectively.

$$\hat{\mu}_j = \frac{1}{N}\sum_{i=1}^{N} \log_{10}(a+bx_{ij}) \quad (1)$$

$$\hat{\sigma}_j^2 = \frac{1}{N}\sum_{i=1}^{N} \{\log_{10}(a=bx_{ij}) - \hat{\mu}_j^2\} \quad (2)$$

where N is the number of the rivers.

Similarly, let y_{ij} denote the average of the concentration of k independent measurements on the j-th metal of the i-th downstream river. Then, we introduce Z_{ij} as the following expression.

$$Z_{ij} = \frac{\log_{10}(a+by_{ij})}{\hat{\sigma}_j} \quad (3)$$

Suppose $\log_{10}(a+by_{ij})$ is independently distributed with the same normal distribution $N(\mu_j, \sigma_j^2)$ as that of $\log_{10}(a+bx_{ij})$ for i = 1,2,...,N.

Since N is large, the estimate $\hat{\sigma}^2$ is sufficiently stable and, hence, the j-th column vector of this matrix $Z_{ij} = \{Z_{1j}, Z_{2j}, \ldots, Z_{Nj}\}$ corresponds to the heavy metal H_j (j = 1,2,...,n). This may be considered as a random sample from a normal distribution $N(\mu_j/\sigma_j, 1)$.

Now, we propose the quantity(4) as an index of river pollution. Since Z_{ij} is regarded as a normal distribution $N(\mu_j/\sigma_j, 1)$, and independent of each other for j = 1,2,...,n,

$$t_i = \sum_{j=1}^{n} Z_{ij} \qquad (i=1,2,\ldots,N) \quad (4)$$

t_i will obey a noncentral χ^2- distribution of n degrees of freedom (D.F). $\bar{\chi}^2_{n,\mu^2}$ can be approximated after the method of P.B.Patnaik(1949):

$$\bar{\chi}^2_{n,\mu^2} \simeq c \times \chi^2(f) \quad (5)$$

where $c = \dfrac{n + 2\mu^2}{n + \mu^2}$ and $f = \dfrac{(n + \mu^2)^2}{n + 2\mu^2}$

$\chi^2(f)$ is a central χ^2- distribution of f degrees of freedom and n is the number of heavy metals. By estimating the noncentral parameter $\mu^2 = \sum_{j=1}^{n}(\mu_j/\sigma_j)^2$ from $\hat{\mu}^2 = \sum_{j=1}^{n}(\hat{\mu}_j/\hat{\sigma}_j)^2$ and substituting $\hat{\mu}^2$ into c and f, we can calculate the upper 100% point of the χ^2_{n,μ^2} distribution from which a suitable critical point of pollution will be selected. The following table indicates the critical point of pollution PL(α) for α = 0.05 and 0.1 and selected values of f.

Table 1. PL(α) for α=0.05,α=0.1 for selected values of f*.

f	PL(0.05)	PL(0.1)	f	PL(0.05)	PL(0.1)
1	3.84 x c	2.71 x c	18	28.9 x c	26.0 x c
2	5.99 x c	4.61 x c	19	30.1 x c	27.2 x c
3	7.81 x c	6.25 x c	20	31.4 x c	28.4 x c
4	9.49 x c	7.78 x c	21	32.7 x c	29.6 x c
5	11.11 x c	9.24 x c	22	33.9 x c	30.8 x c
6	12.6 x c	10.6 x c	23	35.2 x c	32.0 x c
7	14.1 x c	12.0 x c	24	36.4 x c	33.2 x c
8	15.5 x c	13.4 x c	25	37.7 x c	34.4 x c
9	16.9 x c	14.7 x c	26	38.9 x c	35.6 x c
10	18.3 x c	16.0 x c	27	40.1 x c	36.7 x c
11	19.7 x c	17.3 x c	28	41 3 x c	37.9 x c
12	21.0 x c	18.5 x c	29	42.6 x c	39.1 x c
13	22.4 x c	19.8 x c	30	43.8 x c	40.3 x c
14	23.7 x c	21.1 x c	40	55.8 x c	51.8 x c
15	25.0 x c	22.3 x c	50	67.5 x c	63.2 x c
16	26.3 x c	23.5 x c	60	79.1 x c	74.4 x c
17	27.6 x c	24.8 x c	70	90.5 x c	85.5 x c

*If f is not an integer, it can be calculated by interpolation.

RESULTS AND DISCUSSION

We obtained random samples of upstream sediment not polluted by waste water and of the downstream sediment by means of an Ekman-Burge dredge at ten points from both sides of 92 rivers in Japan. The pont at which the upstream sediments were taken is not populated and those for the downstream sediments were about 1 km from the mouth of the river. Each of these sediments was stirred well and dried at 80°C. We used 15g of the dry sediments which passed through a 20-mesh sieve and measured the quantities of heavy metals soluble in 0.5N-HCl. We used the quantities of heavy metals soluble in dilute hydrochloric acid because nongeological metals are more easily extracted than metals contained as minerals(Tada et al.1976).

We took a=0 and b=1 in $\log_{10}(a+bx_{ij})$ and measured the acid soluble quantities x_{ij} of Cu,Cr,Zn,Pb and Ni in the upstream sediments obtaining each $\hat{\mu}_j$ and $\hat{\sigma}_j$ from expressions (1) and (2). The results are shown in Table 2.We obtained the critical point of pollution on the bases of Table 2, and the pollution index t of each river with the quantity(4). On the next page We show the calculations used to drive the pollution index of each river in Table 4. In order to compare these rivers with water pollution areas which have been reported in 1971(NHK Local news section,1971) a map of these rivers is shown in Figuer 1.

Table 2. $\hat{\mu}$ and $\hat{\sigma}$ of each heavy metal in upstream sediment.

Metal	Cu	Cr	Pb	Zn	Ni
$\hat{\mu}$	1.689	-0.160	1.798	2.506	0.216
$\hat{\sigma}$	0.742	0.992	0.835	0.827	0.917

(1) In the case of one heavy metal, Cu:

$\mu^2 = (\mu_j/\sigma_j)^2 = 5.181 \quad c = 11.36/6.18 = 1.84 \quad f = 3.36$

Since f is not an integer, PL should be calculated by proportional allotment from Table 1:

$\chi^2_{0.05}(f=3.36) = 8.41$.Thus, the ceitical point of pollution of Cu(PL) is : $8.41 \times c = 8.41 \times 1.84 = 15.47$.

In the same way as with Cu, we can calculate the PL of each heavy metal (i.e. Zn , Pb, Cr and Ni). the results are shown in Table 3.

Table 3. PL of each heavy metal.

Metal	Cr	Zn	Pb	Ni
PL	3.84	22.84	14.37	3.84

(2) In the case of three heavy metals, Cu,Cr and Pb:

$\mu^2 = \sum_{j=1}^{3} (\mu_j/\sigma_j)^2 = (5.18)_{Cu} + (0.026)_{Cr} + (4.590)_{Pb} = 9.795.$

$c = (3 + 19.594)/(3 + 9.795) = 1.77$

$f = (12.797)^2/22.594 = 7.248$

$\chi^2_{0.05}(f=7.25) = 14.45$. Thus, the critical point of pollution for Cu, Cr and Pb (PL) is: $1.77 \times 14.45 = 25.58$.

(3) In the case of five heavy metals, Cu,Cr,Pb,Zn and Ni:

$$\mu^2 = \sum_{j=1}^{5} (\mu_j/\sigma_j)^2 = (5.181)_{Cu} + (0.026)_{Cr} + (4.590)_{Pb} + (9.204)_{Zn} + (0.055)_{Ni} = 19.056.$$

$c = (5 + 38.112)/(5 + 19.056) = 1.79$

$f = (24.056)^2/43.112 = 13.42$

$\chi^2_{0.05}(f=13.42) = 22.92$. Thus, the critical point of pollution for Cu,Cr,Pb,Zn and Ni (PL) is: $1.79 \times 22.42 = 41.02$.

The method stated above is applicable not only to heavy metals of river sediment, but also to BOD, COD, dissolved oxygen, etc., in the water.

Table 4. The pollution index t_i obtained from one, three and five heavy metals.

Samp. No.	River	Cu	Cu,Cr,Pb	Cu,Cr,Pb, Zn,Ni
1	Teshio	9.63	13.34	30.30
2	Ishikari	24.71*	40.09*	73.47*
3	Shiribetsu	4.70	9.79	23.92
4	Mu	2.19	4.83	19.96
5	Saru	7.85	13.52	28.99
6	Tokachi	8.76	12.48	20.97
7	Shinkushiro	2.19	2.19	46.94*
8	Yubetsu	4.70	7.49	24.04
9	Abashiri	7.85	13.28	31.63
10	Tokoro	9.63	14.72	30.53
11	Iwaki	19.73*	38.05*	68.88*
12	Omono	18.81*	30.82*	58.01*
13	Aka	0.00	1.73	10.13
14	Mabuchi	23.68*	46.63*	90.97*
15	Kitakami	46.78*	66.32*	123.79*
16	Naruse	0.87	3.62	15.36
17	Abukuma	9.63	15.54	44.40*
18	Kuji	15.17	25.83*	46.79*
19	Tone	23.68	38.45*	68.62*
20	Ara	5.83	13.06	35.77
21	Tama	25.69*	56.31*	103.44*
22	Tsurumi	46.08*	87.37*	159.86*
23	Sagami	17.35*	26.08	41.49*
24	Ara	2.19	9.79	21.53
25	Agano	3.49	8.92	24.44
26	Shinano	37.66*	66.61*	119.04*
27	Seki	15.74*	32.48*	56.33*
28	Kurobe	3.49	5.22	13.71
29	Jintsu	17.35*	40.97*	92.65*
30	Jyoganji	0.00	0.68	9.09
31	Syo	28.07*	51.88*	85.30*
32	Koyabe	25.69*	54.22*	98.79*
33	Tedori	4.70	10.13	20.31
34	Takahashi	64.98*	91.06*	147.67*
35	Kuzuryu	7.85	18.87	46.52*
36	Kiku	15.17	23.26	47.53*
37	Fuji	14.58	24.50	61.89
38	Kano	23.68*	41.08*	68.73*
39	Abe	18.81*	22.53	32.99
40	Oi	5.83	12.03	22.75
41	Tenryu	9.63	13.83	24.29
42	Yahagi	0.87	1.56	7.09
43	Toyo	3.49	4.18	9.44
44	Syonai	29.69*	59.43*	112.63*
45	Kiso	3.49	9.69	24.84
46	Nagara	3.49	13.54	37.01

Samp. No.	River	Cu	Cu,Cr,Pb	Cu,Cr,Pb, Zn,Ni
47	Yura	9.63	16.32	34.90
48	Suzuka	5.83	9.07	23.18
49	Shingu	2.19	5.90	12.23
50	Kumozu	0.00	0.00	0.72
51	Kongo	0.87	3.62	11.38
52	Kino	35.68*	73.81*	131.96*
53	Yamato	18.34*	44.68*	85.99*
54	Kako	10.44	24.59	49.81*
55	Ote	0.00	0.69	26.02
56	Sendai	21.41*	36.29*	62.48*
57	Maruyama	5.83	18.30	36.82
58	Tenjin	2.19	3.92	14.64
59	Hino	2.19	2.88	11.91
60	Hii	4.70	6.43	8.20
61	Takatsu	8.76	20.28	32.09
62	Saba	2.19	2.88	6.66
63	Koze	0.00	0.68	5.38
64	Ashida	22.20*	39.38*	74.20*
65	Takahashi	11.21	23.46	51.64*
66	Asahi	22.95*	44.88*	88.30*
67	Yoshii	22.20*	39.35*	80.28*
68	Ota	29.68*	68.88*	130.03*
69	Hiji	28.90*	42.73*	71.18*
70	Niyodo	10.44	17.13	34.18
71	Monobe	5.83	8.78	19.48
72	Naka	8.76	18.69	49.93*
73	Doki	7.85	18.86	40.98
74	Shimanto	6.87	14.29	29.34
75	Yoshino	10.44	16.36	28.17
76	Onga	0.00	0.68	7.58
77	Okibata	10.44	26.10*	61.78*
78	Oita	8.76	17.64	42.04*
79	Ono	0.00	0.68	27.82
80	Bansho	8.76	17.60	33.35
81	Gokase	9.63	26.04*	64.34*
82	Komaru	18.81*	36.50*	65.72*
83	Oyodo	13.96	24.04	39.88
84	Kimotsuki	11.21	14.93	27.60
85	Sendai	0.00	0.00	1.76
86	Kuma	11.21	20.07	34.57
87	Midori	25.69*	40.47*	75.40*
88	Shira	31.17*	43.91*	73.91*
89	Kikuchi	12.65	22.09	45.06*
90	Rokkaku	34.06*	50.79*	88.12*
91	Masuura	5.83	8.58	17.93
92	Honmyo	8.76	25.69*	58.64*

* The value above the critical point of pollution

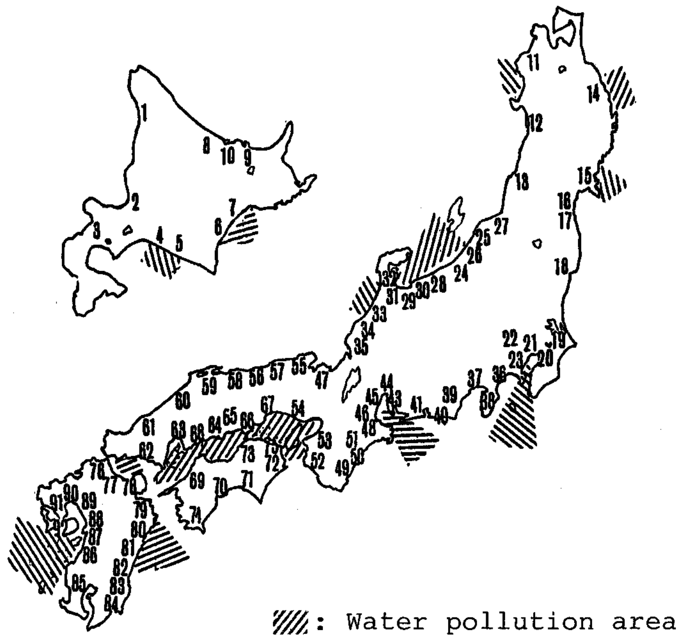

Figure 1. Map of the sampling rivers and water pollution areas.

Acknowledgment. The authors are grateful to S.Ikeda for helpful discussions.

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Received July 26, 1983 : Accepted October 4, 1983