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Industrial Emission of Cadmium in Japan

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Direct emission of cadmium into air and water in Japan has been controlled on the basis of the Emission and Effluent Standards. Environmental quality in these media has been improved, but delayed effects of these emissions in the past are now manifest by contamination of agricultural acreage in various parts of this country. Special land improvement projects are therefore required, and cost allocation should be made on the basis of scientific assessment of natural background. An impact assessment on accidental release of potential sources of cadmium dispersed in the water system should be made on the basis of inventory surveillance.

Assessment of natural background can practically be made by two means. One is to examine the vertical distribution of cadmium in a soil profile and to search for a subsurface layer in which there can be no contamination. Another is the use of the Zn/Cd ratio as an index of pollution, a value of 400 being suggested as a screening level. The transport of cadmium was found to occur principally in particulate form, and sampling and analysis of water together with suspended solid after a heavy rainfall is suggested as a useful means for assessing the character of a catchment area and for planning the improvement of land surface in mining districts.

Introduction

In Japan, as a result of various control measures, including the first establishment of the Basic Law for Environmental Pollution Control in 1967, socioeconomic changes took place in every sector of industry, and the metal mining industry gradually cut down its activities. Figure 1 shows decreasing trends in the shipping ore production in this country. Particularly in the case of mercury, domestic production decreased to practically zero in 1975. It should be noted that production of shipping ores is different from metal production, since the latter can be made on the basis of imported shipping ores.

Cadmium is a by-product of zinc processing, and the refining capacity of cadmium metal in Japan was about 3000 tons per year in 1973. This capacity is about one sixth of the world production, and actual production of cadmium metal in this country remains almost on the same level in these years. A shortage in raw materials, namely the zinc shipping ores, was covered by increases in imported materials. In fact, only 3.3% of the demand depended on import but the figure increased to 58.4% in 1972.

The domestic demand for cadmium metal has been decreased on taking into consideration the enforcement of control measures. Necessarily, the export of excess cadmium has increased in these years as shown in Figure 2. As a whole, domestic use of cadmium decreased by about 60% from 2253 tons in 1969 to 927 tons in 1974. The latter amount is approximately one sixth of the 12.5 million pounds used in the United States. Another difference between two countries is found in the pattern of usage. Almost half of this amount in the United States was used in the metal finishing industry, while almost half of that in Japan was used for pigments and plastic

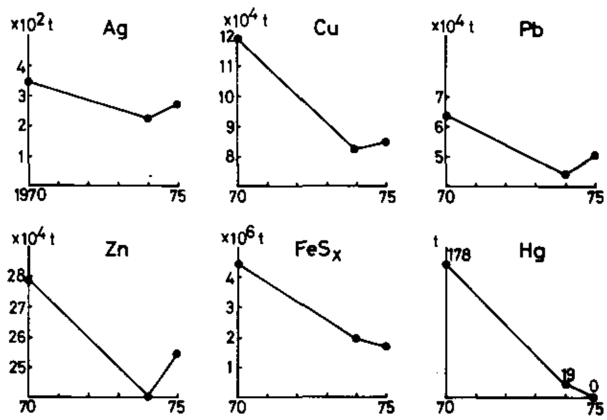

FIGURE 1. Decrease in the production of shipping ores in Japan (1970-197!

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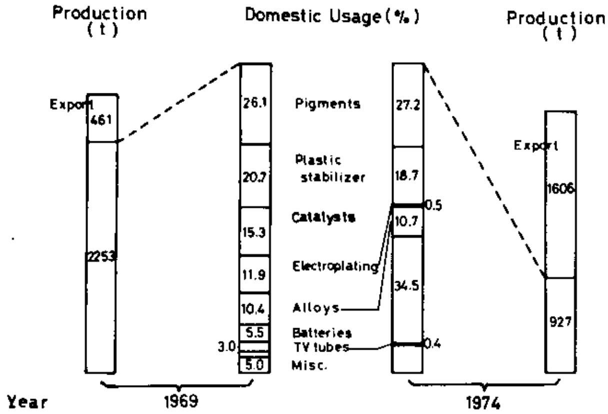

FIGURE 2. Production and domestic usage of cadmium metal in Japan (1969 and 1974).

stabilizers in either of 1969 and 1974. A great change in the usage pattern in Japan in five years (1969-1974) can be seen; it suggests a reflection of pollution control guidance and technical innovation. Namely, use as catalyst, in electroplating, and TV tubes showed marked decreases. For example, cadmium used as catalyst decreased from 267 tons in 1969 to only 5 tons in 1974, but in batteries a marked increase is found.

Cadmium pollution of the environment in Japan has occurred as contamination of agricultural land directly by fallout from aerial emission or indirectly by water transport of sludge in particulate form. An example of the former is in the case of Annaka City, Gunma Prefecture, and of the latter Jintsu River basin, Toyama Prefecture, in which Itai-itai disease outbroke. Contamination of waters by cadmium has also been observed in 2.8% of total surveyed cases in 1970; this proportion decreased to 0.31% in 1975 (Table 1), but real and long-term effect of such contamination should be comparatively small as compared with those of land contamination now manifested as the result of previous industrial activities.

Main Problems in the Environment

In recent years, the contamination of agricultural land by cadmium and other elements has been noted in various parts of the country. A close investigation in 1975, officially called the Close Survey to Counter Soil Pollution, was carried out for cadmium in 138 areas of 34 prefectures totalling 10,900 ha; amounts in excess of standard values were detected in 22 areas. A maximum cadmium concentration in rice of 4.04 ppm was recorded in the left bank area of the Jintsu River.

Table 1. Cases in which cadmium contents exceeded the Environmental Water Quality Standard (0.01 ppm).

Year	Number of cases surveyed (*A*)	Number of cases exceeding the standards (*B*)	Ratio *B*/*A*, %
1970	2,564	71	2.8
1971	15,944	114	0.7
1972	27,951	95	0.34
1973	30,567	98	0.32
1974	31,915	119	0.37
1975	32,851	103	0.31

In view of this situation, the present paper describes the emission and dispersion of cadmium, especially via water. The present and future problems of environmental pollution by cadmium in this country in connection with mining and refining activities can be summarized as follows. The first problem is concerned with the improvement of polluted agricultural land. Control of direct emission of cadmium into air and water can be made on the basis of such regulations as the Emission Standards and Effluent Standards summarized in Table 2. In contrast, countermeasures for already polluted agricultural land must be taken by such special land improvement undertakings as removal or replacement of topsoil. Such action requires a vast sum of money, and cost allocation should be raised as a question among polluters and local and central governments, because in some cases several mining companies may be involved.

A rule for cost allocation now generally accepted is based on the concept that the amount of cadmium in surface soil of the agricultural land concerned (A) in excess of natural background of the area (B) should have been contributed by polluters ($A - B$) and when the background is higher than the national average (0.4 ppm, see Table 3), the difference ($B - 0.4$) should be considered by government. The cost allocation will be determined in proportion, with some modification, to $A - B$ and $B - 0.4$. Then, the assessment of the natural background of the area concerned remains; the responsibility of resolving this question lies with the scientists, including the geochemists. Allocation mediation has been made on the local government level, and the total cost of improvement enterprises in ten areas amounted to about 10 billion yen as of September 1977; the average allocation to polluters was 52.5%.

The second problem is concerned with the impact assessment on accidental releases. As the result of mining and refining activities in the past, potential sources of cadmium are scattered everywhere in the river system concerned: for example, in the riverbed, the settling basin, and the erosion control dam. In a dam collapse occurring last year at the

Table 2. Environmental standards for cadmium and its compounds in Japan.

Standard	Facility	Standard value or permissible limit
Emission Standards (Harmful Substances June 22, 1971)	Baking furnace and smelting furnace for manufacturing glass using cadmium sulfide or cadmium carbonate as raw material	1.0 mg/Nm^3
	Calcination furnace, sintering furnace, smelting furnace, converter and drying furnace for refining copper, lead or cadmium	1.0 mg/Nm^3
	Drying facility for manufacturing cadmium pigment, or cadmium carbonate	1.0 mg/Nm^3
Effluent Standards (June 21, 1971): Substances related to the Protection of Human Health	——	0.1 mg/l.
Environmental Water Quality Standards (Dec. 28, 1971)	——	<0.01 ppm

Table 3. National survey of cadmium in nonpolluted soil (Environment Agency, 1972).

Land category	Number of samples	Cd, ppm	
		Mean ± SD	Maximum
Paddy	2746	0.4 ± 0.5	7.1
Farmland	722	0.3 ± 0.1	1.0
Orchard	268	0.3 ± 0.2	1.2

Table 4. Production record of Yoshino Mine, Nippon Mining Co., Yamagata Prefecture (1955–1973).

Material	Production, tons	Cd, tons	Cd concn, ppm
Crude ores	1,975,794	294.54	149
Shipping ores	517,146	278.89	539
Sludges	1,458,648	15.65	11

Mochikoshi Gold Mine, Shizuoka Prefecture due to an earthquake, a damage was done by cyanide-containing sludge to fishes downstream. Even unusually heavy rainfall may lead to accidental release of cadmium from potential sources. Thus, inventory of potential sources in a river system should be made clear in order to evaluate risks of accidental release.

The largest introduction of cadmium into the environment is considered to be made by the Kamioka Mine, Gifu Prefecture. It is estimated that total production was 10^6 tons of zinc metal from 1874 to 1960 and 4271 tons of cadmium during the same period, of which about 21 tons per year were lost (*1*). Since the allocation mediation related to this mine is still in dispute and final data are not available, only the transport of cadmium by river and background assessment in paddy fields on the basis of data obtained in the Yoshino River basin, Yamagata Prefecture (*2*) will be discussed.

Transport of Cadmium by River

The largest mine in this basin is the Yoshino Mine, Nippon Mining Co. The production record shows that the total production of cadmium was approximately 300 tons, of which about 95% passed into shipping ores, and the difference was lost as sludges (Table 4). Therefore, if the production record is correct, about 16 tons of cadmium should have been lost. This figure is remarkably small as compared with the estimated loss of 21 tons per year at the Kamioka Mine. This great difference is naturally due to great differences in production both in scale and time.

The Yoshino Mine stopped its activity in 1973 and the inventory of potential sources was surveyed in 1974. The results were 4.7 tons of cadmium in 571 hectares of paddy field situated downstream of the Yoshino River, one ton in riverbed, 11 tons in settling basin and 16.7 tons in total. This figure approximates the total loss estimated on the basis of production data, but it should be considered that this coincidence is incidental and the estimated loss is an underestimate, because a part of the cadmium should have been taken away by river flow far downstream and at the same time, the estimated loss of 5% in the dressing process at the Yoshino Mine is too small as compared with the value of about 10% given for the Kamioka Mine.

The transport of cadmium by river was found to occur principally in particulate form, especially at flood stage or after heavy rainfalls. In periods of water shortage, the flow rate at one observation point was as small as 0.1-0.2 m^3/sec, while at flood stage the rate reached 6 m^3/sec and the concentration of suspended solid (SS) reached several hundred parts per million. The runoff of cadmium can be estimated by the following equation:

Runoff Cd (μg/sec) = Flow rate (m^3/sec) × SS (g/m^3 or ppm) × Cd in SS (μg/g or ppm)

The heavy metal concentrations in the suspended solids collected at each of the tributaries of the Yoshino River reflect the character of each respective catchment area, and the runoff of suspended solids in river per unit area of catchment should reflect the extent of land erosion. Sampling points are shown schematically in Figure 3. The river is a very small one, about 15 km in length, and at point J in the catchment area is only 63.6 km^2.

The sampling of water was made after the rainfall, and the result of analyses is summarized in Table 5. There is a wide range of variation of suspended solids and cadmium concentrations among the sampling points. When the precision of analysis is taken into consideration, it can be said that at the lower courses of the main stream (points H and J) the greater part of runoff cadmium is contributed by particulates, while in the tributaries or in the vicinity of the mining activities, the cadmium is predominantly in a soluble form.

Table 6 shows the character of the catchment area in runoff of suspended solids and its cadmium concentrations. The greatest transport of suspended solids occurred at point C, reflecting that the greatest disturbance of land surface by mining activity occurs in this catchment area. At point E, the greatest cadmium concentration in suspended solids and very small suspended solids concentration are observed. In this catchment area, zinc ore dressing by hand-picking was conducted, and mining was abandoned a long time ago. No mining activity has occurred in the catchment of the tributary indicated by I, and the heavy metal concentrations in the suspended solids can be considered as representative of the natural background. At point B, the ratio of

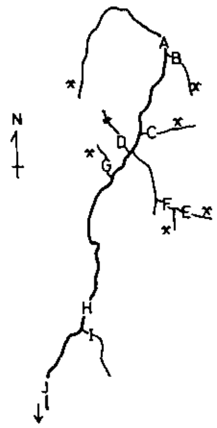

FIGURE 3. Sampling points (A, B, . . ., J) in Yoshino River and its tributaries.

Table 5. Contribution of particulate to total runoff of cadmium in Yoshino River.

Sampling point	Suspended solids, ppm	Cd in suspended solids, ppm	Total Cd in water, ppb[a]	Particulate Cd in water, ppb[b]	Contribution of particulate, %
A[c]	38.6	3.34	0	0.13	—
B	66.8	1.28	2	0.08	4
C	448	4.67	10	2.1	21
D	37.4	16.7	1	0.63	63
E	13.6	63.5	8	0.86	11
F	28.0	3.45	9	0.97	11
G	28.4	2.26	9	0.64	7
H[c]	221	8.15	2	1.8	90
I	129	1.67	0	0.22	—
J[c]	237	8.96	2	2.1	~100

[a] Analysis of unfiltered water.
[b] Calculated by SS (ppm) × Cd in SS (ppm).
[c] Yoshino River main stream; others are tributaries.

Table 6. Character of catchment area reflected by runoff of suspended solids (SS) and heavy metals.

Sampling point	Character	Catchment area, km^2	Suspended solids, g/sec-km^2	Metals, ppm in dry SS			Zn/Cd	Zn/Cu
				Cd	Zn	Cu		
B	Copper-rich ores	1.12	19.6	0.45	179	126	396	1.42
C	Zinc-rich ores	2.31	128.1	6.67	1620	426	243	3.80
E	Zinc-rich ores	0.70	4.0	57.4	3434	868	59.8	3.96
I	No mining activity	2.83	3.5	0.69	189	49.3	274	3.83
J[a]	Whole area	63.60	15.3	8.63	1206	600	140	2.01

[a] Yoshino River main stream.

zinc to copper in the suspended solids is smaller by a factor of more than two than those in other tributaries. This should be a reflection of the fact that in this area copper-rich ores were principally produced.

These findings strongly suggest that the sampling and analysis of suspended solids at the flood stage or after a heavy rainfall is a useful means for planning the improvement of land surface in mining districts and also for assessing different contributions of a number of mines to a combined pollution effect.

Assessment of Natural Background

As stated before, the assessment of natural background is essential for cost allocation, and this natural background means that concentration of cadmium in the agricultural land of concern which would have been found if mining had not been undertaken upstream. Therefore, the assessment of such levels is very difficult.

The simplest idea should be to look for an adjacent area, similar in all respects including geological formation, to the area of concern but in which no mining activity has taken place. Such an area cannot be easily found.

One alternative idea is to examine the vertical distribution of cadmium in the soil of the polluted area and to find out the cadmium concentration in subsurface soil in which contamination cannot take place. One of the disadvantages involved in this method is that cadmium has a tendency to move upward in soil profile. Some investigations on the accumulation of cadmium in the surface layer on the basis of soil profile analysis showed a factor of two on the average, but this factor can not always be applied to a particular soil profile.

In Table 7 is shown an example of vertical distribution of heavy metals in representative polluted and unpolluted areas. The distribution was determined to the depth of 100 cm. In the polluted area, where irrigation water is taken from the Yoshino River, remarkable decreases in heavy metal concentrations and an increase in the Zn/Cd ratio with depth can be seen, while such patterns can not be seen in unpolluted area where irrigation water is taken from another river in which no mining activity has occurred upstream.

On the basis of the data given in Table 7, one can assume approximate values of natural background levels in the polluted area in a layer somewhere deeper than 30 cm, namely, 0.3–0.5 ppm cadmium, about 250 ppm zinc, and about 40 ppm copper. These values can be contrasted to those in the unpolluted area, namely, 0.2–0.3 ppm cadmium, about 100 ppm zinc, and about 15 ppm copper. The difference between the assumed background in the polluted area and observed values in the unpolluted area should be attributable to differences in the natural geological and geochemical characters of the two regions.

Table 7. Comparison of polluted and adjacent unpolluted paddy fields in the vertical distribution of heavy metals.

Locality	Soil depth, cm	Metals, ppm (dry basis)			
		Cd	Zn	Cu	Zn/Cd
Kunugizuka polluted area, irrigation water from Yoshino River	0-15	3.07	549	156	179
	15-30	1.65	417	93.6	253
	30-50	0.677	277	42.2	409
	50-70	0.310	259	40.2	835
	70-85	0.243	234	39.1	962
	85-100	0.212	206	28.5	972
Hanetsuke unpolluted area, irrigation water from Orihata River	0-20	0.283	109	16.7	385
	20-30	0.303	94.1	12.6	311
	50-60	0.144	106	16.4	736
	70-80	0.224	108	10.5	482
	80-90	0.109	99.5	10.7	913
	90-100	0.202	90.2	13.9	447

Table 8. Zn/Cd ratios in soil, deposit, and suspended solids in water in polluted areas.

Locality	Matrix	Range of Zn/Cd or Mean ± SD, ppm
Yoshino River, Yamagata Pref.	Runoff suspended solids at flood stage	56-397
Yamagata Pref.	Bottom deposit at Sakamachi Dam	196 (±14%)
Yamagata Pref.	Bottom deposit at Taro Dam	220 (±15%)
Yamagata Pref.	Bottom deposit at Kunugizuka	221-254
Yamagata Pref.	Bottom deposit in irrigation waterways	202-370
Yamagata Pref.	Bottom deposit in mine effluents	180-394
Jintsu River, Toyama Pref.	Paddy soil	142-364
Tsushima, Nagasaki Pref.	Paddy soil	135-316
Okudake River, Oita Pref.	Paddy soil	76-184
Annaka City, Gunma Pref.	Paddy soil	49-142

Another means of assessing natural background cadmium levels is the use of the ratio of zinc to cadmium in soil as an index of pollution. The Zn/Cd ratio for the lithosphere is calculated to be 900 according to the Clarke number. The median ratio for normal soils is reported by Vinogradov as 1400, ranging from 180 to 12,000. Marine sediment in the Japan Sea off Toyama City also showed 1300–1400. The collection of such data and the fact that, in the

Jintsu River basin, the ratios in the polluted field were 142–364 in contrast to larger values (430–1600) in normal areas upstream from the mine (*3*) suggests the possible use of the ratio as a screening parameter for pollution. The data summarized in Table 8 indicate that all the values in soil, runoff suspended solids, and bottom deposit are less than 400, irrespective of locality and matrix.

On the assumption that the Zn/Cd ratio in normal or not polluted soil should be 400 or larger, some information on the natural background concentration of cadmium in soil can be derived from a series of analytical data for zinc and cadmium. This method was applied to the Yoshino River basin and the results were as follows. Of 63 samples collected from the ground surface of the mining district, 20 samples showed a Zn/Cd ratio larger than 400, ranging from 434 to 1296, 644 on the average, and at the same time the cadmium concentration ranged from 0.11 to 0.63 ppm, the average being 0.25. In the same way, of 71 analytical data of the 13 plots in polluted paddies, 16 samples showed a Zn/Cd ratio larger than 400. The cadmium concentration ranged from 0.21 to 0.68 ppm, the average being 0.45 ppm and the Zn/Cd ratio ranged from 409 to 972, the average being 580.

The total amount of cadmium artificially introduced into the agricultural land to the depth of 30 cm by mining activity was estimated as approximately 3.5 tons by subtracting the amount of natural background from the total. On this basis, the cost allocation has been carried out, with some modifications.

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