Behavior of Chemicals Suspected of EDCs and Other Related Chemicals in Drinking Water Supply

水道における内分泌かく乱化学物質とその他関連化学物質の挙動

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BEHAVIOR OF CHEMICALS SUSPECTED OF EDCs AND OTHER RELATED CHEMICALS IN DRINKING WATER SUPPLY

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ABSTRACT

A study on the behavior of di-2-ethylhexyl phthalate(DEHP) and di-n-butyl phthalate(DNBP) at eleven water treatment plants showed that both DEHP and DNBP could be removed to some extent by water treatment with a rapid sand filtration system. DEHP in raw water tended to be concentrated in sludge and scum more than DNBP in raw water. Another study on their mass balance at three water treatment plants showed that a considerable part of DEHP and DNBP contained in raw water was accumulated in sludge at a water treatment plant, and that only a limited part of them was concentrated in scum. In addition, it was found as the result of repeated chemical release tests using water pipes coated with tar-epoxy resin paint, which had widely been used, that phthalates, phenols and polyaromatic hydrocarbons(PAHs) were released at the beginning of their use, but that the release of those chemicals would not last for many months.

KEYWORDS

Endocrine disrupting chemicals(EDCs), drinking water treatment, water pipes, di-2-ethylhexyl phthalate(DEHP), di-n-butyl phthalate(DNBP), polyaromatic hydrocarbons(PAHs)

INTRODUCTION

Endocrine disrupting chemicals(EDCs) are of concern among researchers since several years ago. We have been conducting a series of researches on chemicals suspected of EDCs in drinking water. The scope of such researches mainly includes their occurrence in raw and treated waters, their removal and behavior in water treatment processes, their release from water supply materials, and estrogenic activities of their chlorination by-products. At present, we are conducting studies on the behavior of di-2-ethylhexyl phthalate(DEHP) and di-n-butyl phthalate(DNBP) in drinking water treatment, and the release of phthalates, phenols and polyaromatic

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hydrocarbons(PAHs) from tar-based resin paints.

In this paper, the result of such studies on the behavior of EDCs in drinking water supply is reported and discussed.

BEHAVIOR OF PHTHALATES IN DRINKING WATER TREATMENT

Background and objective

Since phthalates, such as DEHP and DNBP, are widely used as the plasticizer of plastics, they often occur in raw water for drinking water supply. They are also released from the materials used for water supply, e.g. water pipes, in contact with water. In our previous study[1)], we found that DEHP existed at a very high concentration of more than 10μg/l in treated water at the top layer of a treated water reservoir of a certain treatment plant. Then, the DEHP and DMBP contents in sludge and scum as well as their concentrations in raw and treated waters at eleven water treatment plants in Japan were investigated for the purpose to know their behavior in water treatment processes. In addition, a more detailed study was conducted at three out of those ten water treatment plants for the purpose to know their mass balance in water treatment processes.

Methods

Samples of water, sludge and scum were taken once at each of eleven water treatment plants in January through February, 2003, and analyzed on DEHP, DNBP and other parameters. Ten treatment plants adopt a rapid sand filtration system, whereas the other one treatment plant adopts a slow sand filtration system. After that, samples of water, sludge and scum were taken again at each of three out of those ten water treatment plants, with a rapid sand filtration system, once a month in January through March, 2004, and analyzed on the same parameters as the previous study. Other data necessary for mass balance analysis such as water flow rate and sludge generation were obtained from each water supply.

Result and discussions

Figure 1 shows the result of analysis on DEHP and DNBP concentrations in raw and treated waters of eleven water treatment plants. Both DEHP and DNBP concentrations in raw water at all treatment plants were less than 1μg/l, and DEHP concentrations in raw water were almost the same as or higher than DNBP concentrations in raw water. Both of the distribution of DEHP and DNBP

concentrations in water shifted to lower ranges after treatment, which means that DEHP and DNBP were removed to some extent.

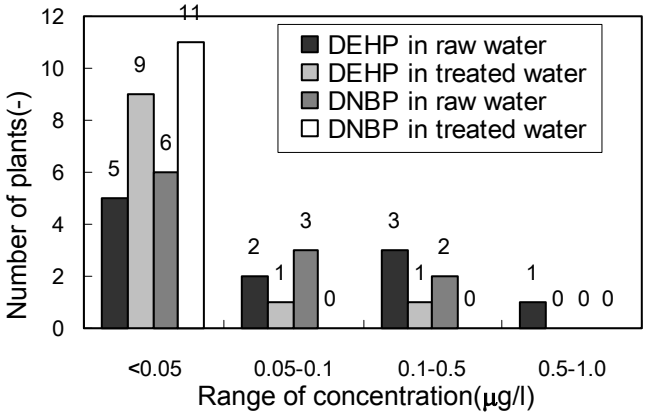

Figure 1 DEHP and DNBP concentrations in raw and treated waters

Figure 2 and 3 show the contents of DEHP and DNBP, respectively, in sludge and scum. Sludge samples were taken only at ten treatment plants with a rapid sand filtration system. Scum samples were taken at the inlet of a sedimentation basin in most plants, but scum was not formed at three of those ten treatment plants. It is clear from these results that both DEHP and DNBP were concentrated not only in sludge but also in scum, and that they tended to be concentrated more in scum than in sludge. The maximum contents of DEHP in sludge and scum were 14 and 52mg/kg dry weight, respectively. The maximum contents of DNBP in sludge and scum were 2.2 and 2.3mg/kg dry weight, respectively. It was also found that DEHP tended to be concentrated in sludge and scum more than DNBP. This might be due to the difference in Kow between DEHP and DNBP.

Figure 4 to 6 show the result of a detailed study on the mass balance of DEHP at three water treatment plants with a rapid sand filtration system. It was found from the result that a considerable part of DEHP contained in raw water was accumulated

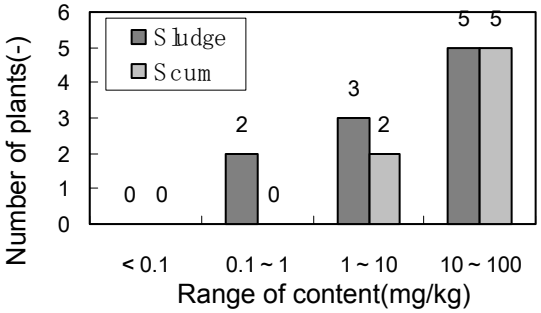

Figure 2 DEHP contents in sludge and scum

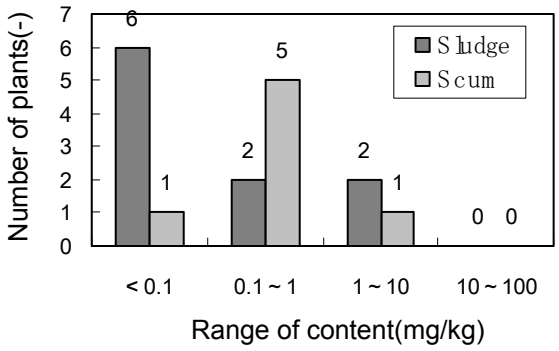

Figure 3 DNBP contents in sludge and scum

in sludge at each treatment plant, and only a limited part of it was concentrated in scum. The result of DNBP mass balance also showed a similar result. One of the treatment plants was typical because the water at a top layer of its treated water reservoir exhibited a very high DEHP concentration at every sampling occasion as was in a previous study[1)]. Such a phenomenon could not be found in other treatment plants.

RELEASE OF PAHs AND OTHER CHEMICALS FROM WATER PIPES

Background and objective

Tar-based resin paints such as tar-epoxy and coal tar enamel resin paints had widely been used for painting the inner wall of water pipes and basins in Japan. Although they are not used since more than ten years ago, it is of concern that they may have a potential of releasing hazardous chemicals, like EDCs, to drinking water[2)]. It is also a matter of concern that the by-product of a reaction of chemicals, which are released

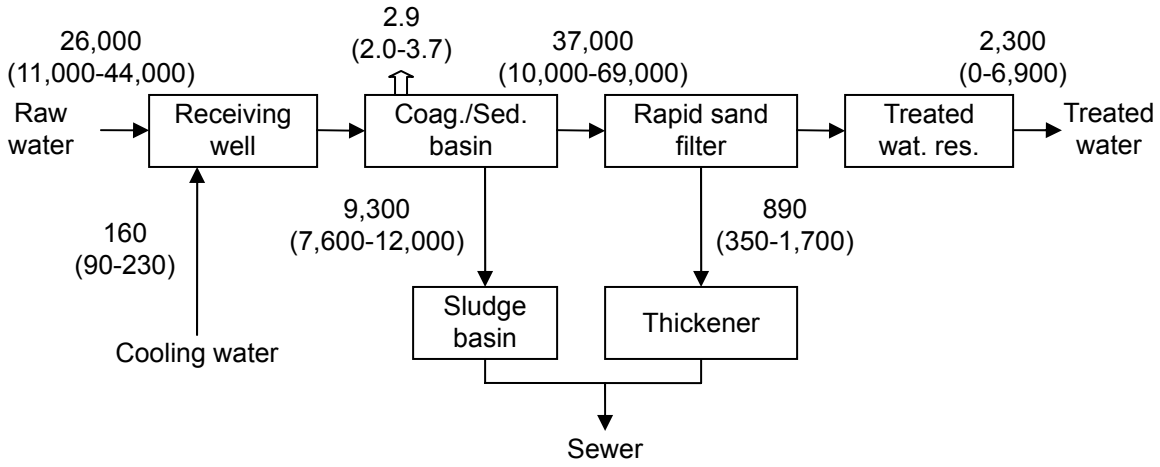

Figure 4 Mass balance of DEHP at "R" water treatment plant(unit: mg/d)

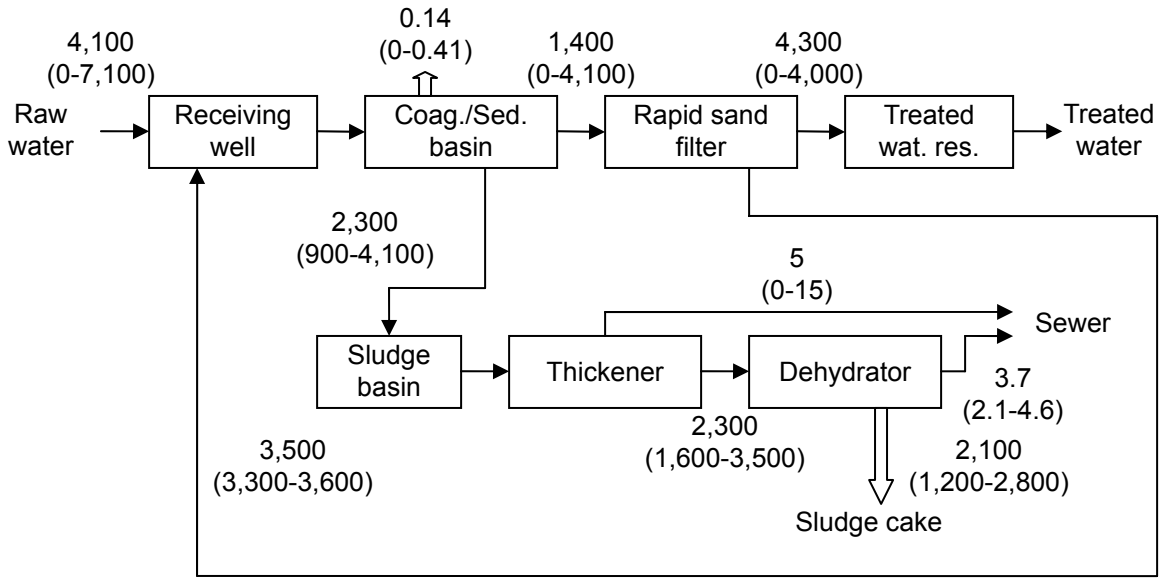

Figure 5 Mass balance of DEHP at "Q" water treatment plant(unit: mg/d)

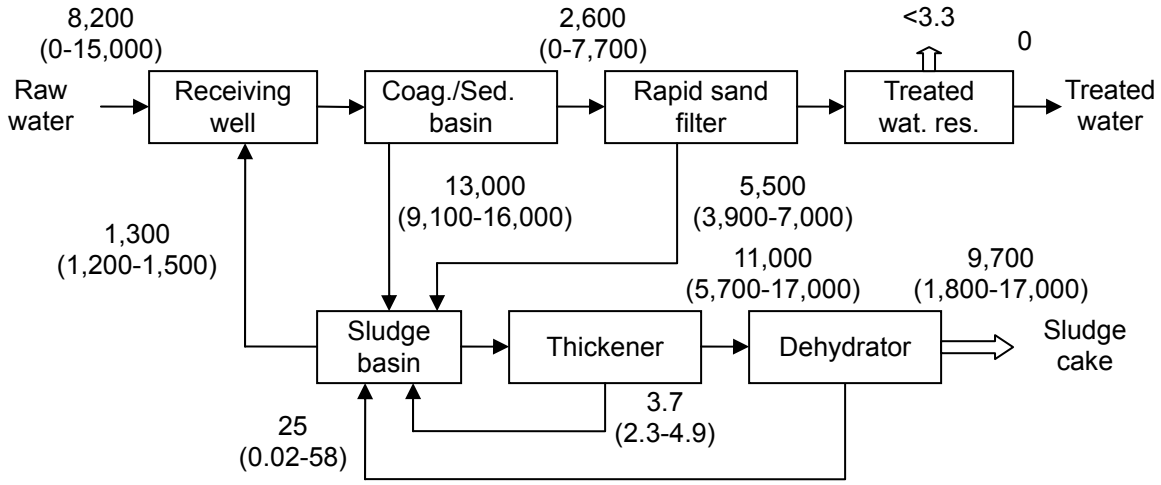

Figure 6 Mass balance of DEHP at "T" water treatment plant(unit: mg/d)

to water, with residual chlorine in water may have a health risk potential as EDCs. Then, a study on the release of chemicals was conducted using samples of water pipes, coated with tar-epoxy resin paint, which were newly produced for the study.

Methods

Two types of new steel water pipes, with an inner diameter of 32mm and 40mm, coated with tar-epoxy resin paint on their inner wall were used for the study. The grade of the paint was same as that used for water pipes in old days. Ten pipes of

each type were installed on a rack, connecting them with each other in line, in a water treatment plant, and continuously supplied with treated water containing residual chlorine at a flow rate of one cubic meter per day in order to simulate a daily use of drinking water. The pipes were removed from the rack and transported to a laboratory for a chemical release test at selected time intervals.

The conditions of chemical release test were as follows: temperature at 23±1°C and contact time for 16 hours. A bland of commercially available mineral water containing minimum concentrations of target chemicals was used for the test without adding chlorine or any other chemicals. A blank test with a similar procedure, but without contact with the pipes, was also done in parallel. Chemicals analyzed on an extract obtained after contact with the pipes and a blank water sample were DEHP, DNBP, nonylphenol, bisphenol A, and PAHs. If the difference in the concentrations of each chemical between an extract and a blank water sample after a similar procedure was not less than the lower limit of release detection for each chemical, it was considered that its release had occurred. The lower limit of release detection for each chemical was determined through a statistical analysis of the result of blank tests separately done. After finishing the test, the pipes were transported back to the water treatment plant, reinstalled on a rack, and continuously supplied with treated water.

Result and discussions

Table 1 shows the result of chemical release tests during six months from the start of this study. The release of many kinds of chemicals from both types of water pipes was observed at the beginning. The concentrations of DNBP and fluoranthene in a water sample after contact with 32mm pipes were more than 1μg/l, whereas those of others chemicals were less than 1μg/l. The concentrations of all chemicals in a water sample after contact with 40mm pipes were also less than 1μg/l. The concentrations of all selected chemicals in the extract obtained after contact with both types of pipes uniformly decreased until six months after the start of this study. It is considered from such a result that water pipes coated with tar-epoxy resin paint may release chemicals, including phthalates, phenols and PAHs, but the release of those chemicals will not last for many months. It is planned to continue the study until about two years after its start even though significant release of selected chemicals may not occur.

CONCLUSIONS

The main findings of this research on the behavior and mass balance of chemicals

Table 1 Release of phthalates, phenols and PAHs from water pipes coated with tar-epoxy resin paint

Chemical	Lower limit* (μg/l)	Released concentration**(μg/l)					
		At the beginning		After 1 month		After 6 months	
		32mm	40mm	32mm	40mm	32mm	40mm
Di-2-ethylhexyl phthalate	0.4	ND	ND	ND	ND	ND	ND
Di-n-butyl phthalate	0.4	1.4	ND	0.7	ND	ND	ND
Nonylphenol	0.08	0.09	0.10	ND	ND	ND	ND
Bisphenol A	0.01	0.39	0.12	0.04	ND	ND	ND
Benzo(a)pyrene	0.01	ND	0.01	ND	ND	ND	ND
Benzo(a)fluoranthene	0.01	0.02	0.02	0.02	0.01	ND	ND
Fluoranthene	0.01	1.2	0.58	0.60	0.18	0.08	0.04
Benzo(a)antracene	0.01	0.04	0.03	0.02	ND	ND	ND
Pyrene	0.01	0.67	0.38	0.20	0.05	0.01	ND
Chrysene	0.01	0.11	0.12	0.07	0.04	0.02	ND

*) The lower limit of release diction. If the difference in the concentrations of each chemical between an extract and a blank water sample was not less than this value, it was considered that the release of a chemical had occurred.

**) The difference in the concentrations of each chemical between an extract and a blank water sample.

suspected of EDCs are as follows:

1) Both DEHP and DNBP can be removed to some extent by water treatment with a rapid sand filtration system.
2) DEHP in raw water tends to be concentrated in sludge and scum more than DNBP in raw water.
3) A considerable part of DEHP and DNBP contained in raw water is accumulated in sludge at a water treatment plant, and only a limited part of them is concentrated in scum.
4) Water pipes coated with tar-epoxy resin paint, which were widely used, release phthalates, phenols and PAHs, but the release of those chemicals will not last for many months.

ACKNOWLEDGMENT

This study is supported by a Health and Labor Sciences Research Grant in FY2002-2004. The authors express sincere gratitude to local water supplies for contributing to the sampling of water, sludge and scum, and to steel water pipe manufacturers for providing water pipe samples.

REFERENCES

1) S. Kunikane, *et al.*(2002) A report on the behavior of EDCs in drinking water and the measures against drinking water contamination with them(*in Japanese*).
2) World Health Organization(1996) Guidelines for Drinking-water Quality, 2nd edition, Vol.2: Health criteria and other supporting information.

Behavior of chemicals suspected of EDCs and other related chemicals in drinking water supply

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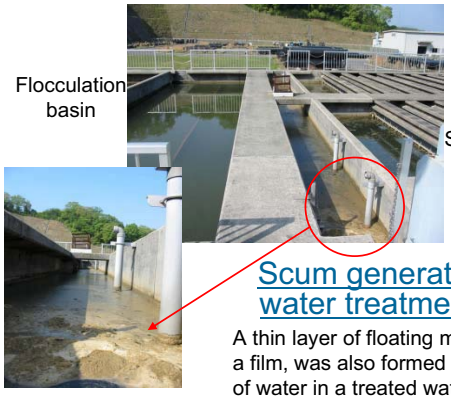
Main scope of studies on EDCs in drinking water supply

- Occurrence in raw and treated waters
- Removal and behavior in water treatment processes
- Release from water supply materials
- Estrogenic activities of chlorination by-products

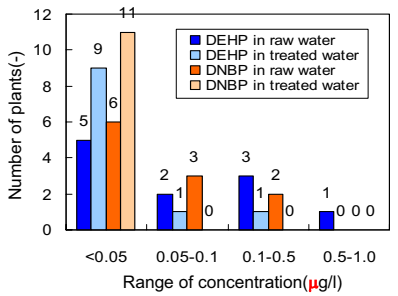
Main subjects of this study

- Behavior of di-2-ethylhexyl phthalate(DEHP) and di-n-butyl phthalate(DNBP) in drinking water treatment
- Release of phthalates, phenols and polyaromatic hydrocarbons(PAHs) from tar-based resin paints



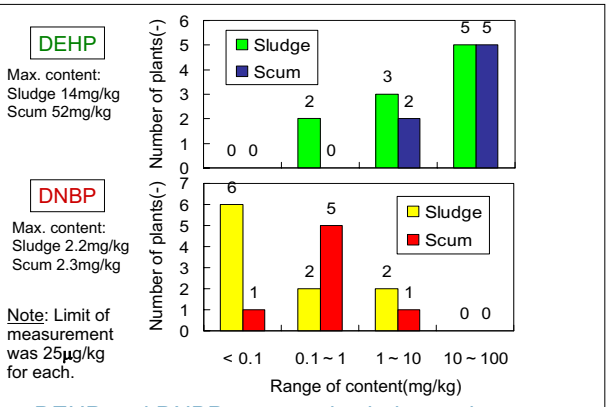
Scum generation at a water treatment plant

A thin layer of floating materials, like a film, was also formed at the surface of water in a treated water reservoir at a certain treatment plant.



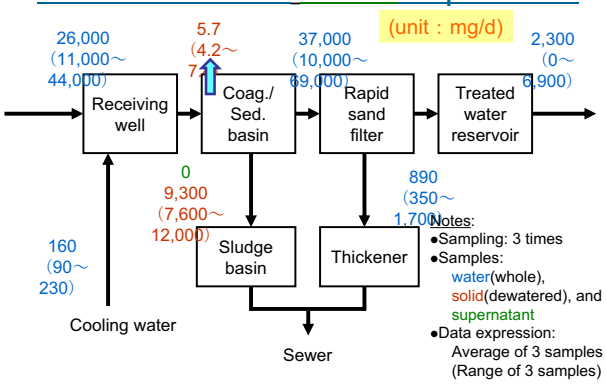
DEHP and DNBP concentrations in raw and treated waters at 11 water treatment plants*

*10 rapid and 1 slow sand filtration plants.
Note: Limit of measurement was 0.05μg/l.

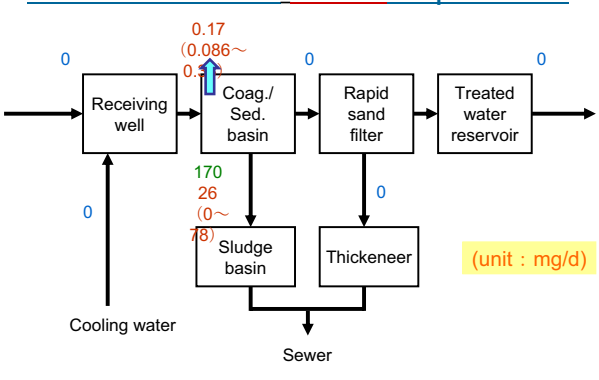


DEHP and DNBP contents in sludge and scum at 11 water treatment plants

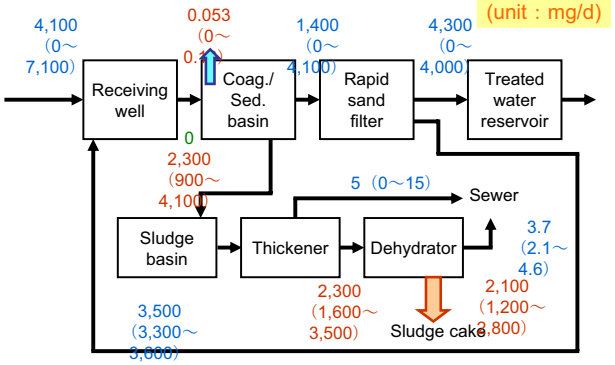
Mass balance of DEHP at plant "R"



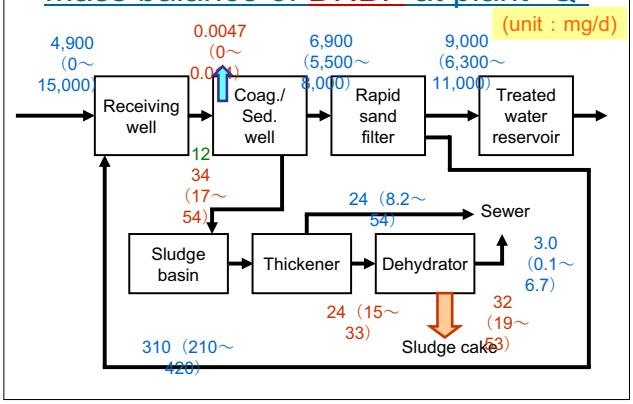
Mass balance of DNBP at plant "R"



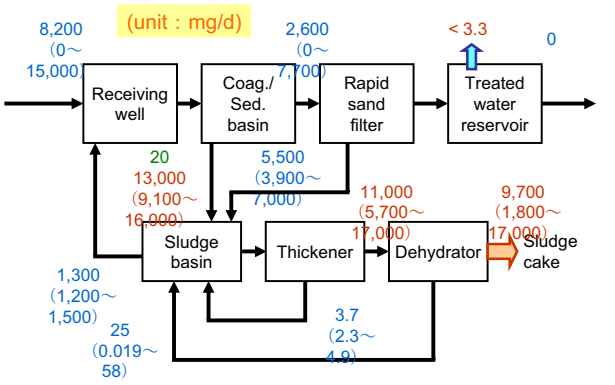
Mass balance of DEHP at plant "Q"



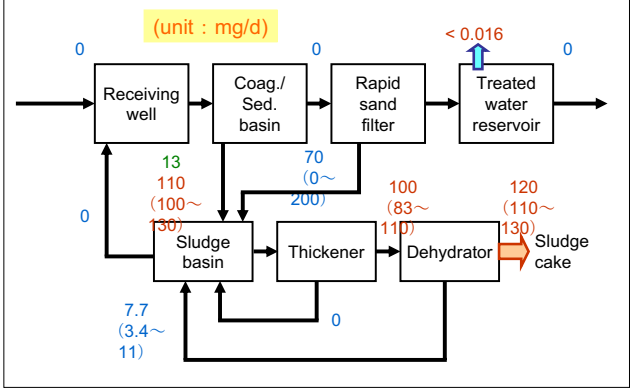
Mass balance of DNBP at plant "Q"



Mass balance of DEHP at plant "T"



Mass balance of DNBP at plant "T"



Set-up of steel water pipes coated with tar epoxy resin paint（ϕ32 and 40mm） which were continuously supplied with treated water containing residual chlorine

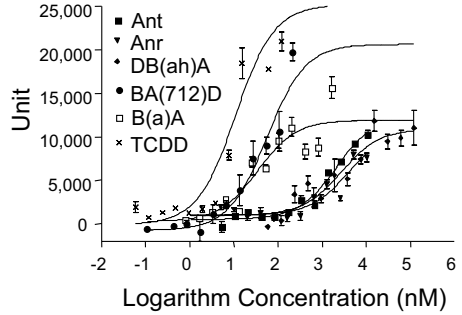
Release of phthalates, phenols and PAHs from water pipes coated with tar-epoxy resin paint

(unit : μg/L)

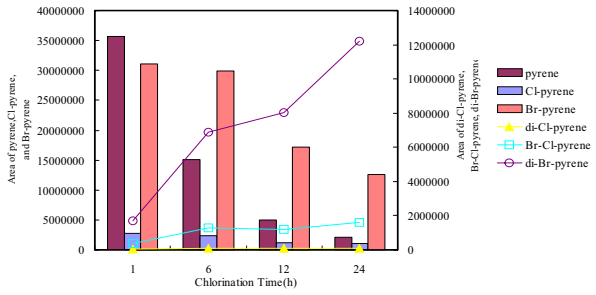
Chemical	Lower limit	0 month	1 month	6 months
DEHP	0.4	- / -	- / -	- / -
DNBP	0.4	1.4/ -	0.7/ -	- / -
Nonylphenol	0.08	0.09/0.10	- / -	- / -
Bisphenol A	0.01	0.39/0.12	0.04/ -	- / -
Benzo(a)pyrene	0.01	- /0.01	- / -	- / -
Benzo(b)fluoranthene	0.01	0.02/0.02	0.02/0.01	- / -
Fluoranthene	0.01	1.2/0.58	0.60/0.18	0.08/0.04
Benzo(a)anthracene	0.01	0.04/0.03	0.02/ -	- / -
Pyrene	0.01	0.67/0.38	0.20/0.05	0.01/ -
Chrysene	0.01	0.11/0.12	0.07/0.04	0.02/ -

Note) Pipe diameters were 32 and 40mm. Test conditions; temperature at 23℃ for 16 hours.

AhR binding activities of anthracenes

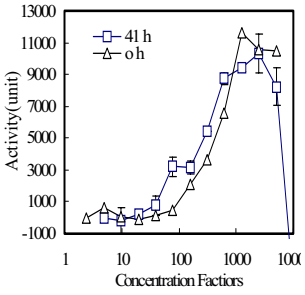


BA(712)D: benz(a)anthracene-7,12-dione
B(a)A: benz(a)anthracene

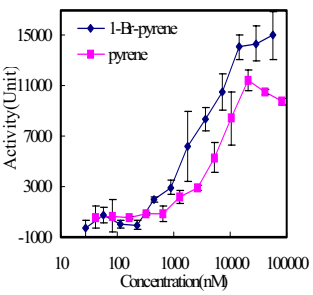


Time-dependent changes in the concentrations of chlorination by-products of pyrene in the existence of bromides

[Br]=1mg/l, [NaOCl]=1.6mg/l, pH=7.22, temperature at 25℃



Change in AhR binding activity of pyrene by chlorination under the existence of bromides



AhR binding activity of pyrene and 1-Br-pyrene standard solutions

Conclusions

1) Both DEHP and DNBP can be removed to some extent by water treatment with a rapid sand filtration system.
2) DEHP in raw water tends to be concentrated in sludge and scum more than DNBP in raw water.
3) A considerable part of DEHP and DNBP contained in raw water is accumulated in sludge at a water treatment plant, and only a limited part of them is concentrated in scum.
4) Water pipes coated with tar-epoxy resin paint, which were widely used, release phthalates, phenols and PAHs, but the release of those chemicals will not last for many months.

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Thank you for your attention!