

How to use the groundwater resources at the area polluted by organoarsenic compounds for Old Japanese Army Toxic Gas Weapon in Japan

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Abstract: We have many problems how to use the ground water resources in geo-pollution sites from a view point of medical geology in Japan. The concept of geo-pollution science as a science in medical geology and the successful continual usage of agricultural ground water in geo-pollution sites due to organoarsenic compounds, e.g. diphenylarsinic acid (DPAA), is shown in the paper.

Key words: geo-pollution; medical geology; organoarsenic compounds; Toxic Gas Weapon; Strata pollution; ground water pollution; ground air pollution

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1 Introduction

Water problems in the world are serious from a point of medical geology because of water pollution problems, e.g. groundwater pollution problem^[1]. We have duty to supply clean water to human-being without chemical disease.

Geo-pollution Science in Medical Geology^[2] plays an important role how to use Geo-environmental Resources, e.g. Groundwater resources, in Geo-pollution area all over the world. Accordingly, we should describe the following successful sustainable usage of agricultural ground water in geo-pollution

sites due to organoarsenic compounds, e.g. diphenylarsinic acid (DPAA).

2 Concept of gepollution—compound pollution that arises from three different types of pollution

“Geo-pollution” is a compound subterranean (underground) pollution comprised of three types of underground pollution: “strata pollution”, e.g. pollution of top soil layer, “groundwater pollution” and “ground air/gas pollution.” These three types of underground pollutions have a complex interaction with each other. Most geo-pollution cases are not

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contained only within surface strata such as man-made strata or top soil layers, but the pollutants usually spread into deeper layers. Consequently, an examination and cleanup of a single medium is not sufficient to solve the problem^[3].

2.1 Strata pollution

Strata pollution typically involves heavy metals (e.g., lead, cadmium, hexavalent chromium, arsenic), volatile organic compounds (VOCs, such as tetrachloroethylene (PCE) and trichloroethylene (TCE)), agricultural chemicals and dioxins. Heavy metal pollution is often found in former sites of chemical factories or plating factories in urban areas, and near waste disposal sites or old mines in suburbs. Organochlorinated substances, once used in large quantity as a degreasing solvent and cleaner by semiconductor factories, mechanical manufacturing and metal processing are found in the areas near those facilities all over Japan. Pollution with agricultural chemicals is common in golf courses as well as in the areas adjacent to farm land. These chemicals tend not to stay in the surface layers including soil layers, and regularly seep into groundwater in aquifer. Dioxin pollution occurs in the strata under and around waste incineration facilities.

2.2 Groundwater pollution

Groundwater pollution threatens one of the most important water sources in our country. As is the case of strata pollution, typical pollutants include heavy metals, organochlorinated substances and agricultural chemicals. There are many incidents of elevated nitrate nitrogen levels in groundwater all over Japan, caused by excessive fertilization and drainage from livestock farming. Compared to other subsurface mediums, groundwater flows and moves the contaminants much faster, spreading the pollution to wider areas within a short period of time. Accordingly, groundwater pollution requires prompt determination of pollution mechanisms to develop containment and cleanup plans in time.

2.3 Ground air pollutions

Ground air pollution occurs when contaminants such as organochlorines, hydrocarbons and

methylmercury are volatilized and released from polluted surface layers and groundwater, and diffuse into ground air inside soil particles or in underground openings. A severe case of ground air pollution can even cause atmospheric pollution. In other cases, surface crop was damaged or died due to ground gas contamination with methane released from landfills and natural gas field.

3 Medical geology and aquifers polluted by organoarsenic compounds for Old Japanese Army Toxic Gas Weapon

Ground water for drinking water of the apartment building contained diphenylarsinic acid (DPAA) (Fig. 1) in Kamisu city, Ibaraki prefecture, Japan. DPAA seems to be the raw materials for Toxic Gas Weapon of Old Japanese Army.

The characteristics of the acid poisoning include brainstem-cerebellar and cerebral symptoms^[4].

After that, phenylarsonic acid (PAA) which may be a degradation product of DPAA is detected in the ground water. Both organoarsenic compounds are detected in groundwater and top soil layer in the paddy field in 2 km from A area (paddy field filled cement milk after being mixed with DPAA and cement) to B area (This study area)^[5-6]. To have the sustainable pumping without the compounds, the pumping and observation well system is set as follows (Fig.2).

In the area, three main aquifers are developed with the sub-aquifers intercalated among each aquifer. The groundwater in middle and upper aquifers is not polluted by both organoarsenic compounds but polluted in lower aquifer^[7]. The concentration of both compounds and total arsenic in each aquifer at the Kamisu observation wells No.1 (Fig.1) is shown in

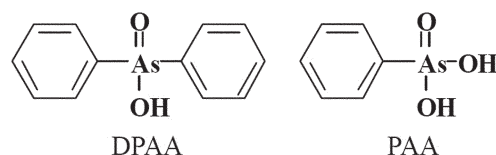


Fig.1 Molecular structure of DPAA and PAA

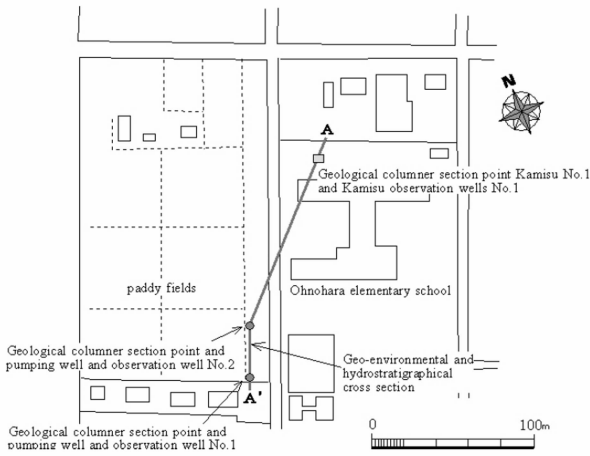


Fig.2 Distribution map of each well and geo-environmental and hydrostratigraphic cross section of A-A' line [7]

Table 1. The former is analyzed by High Performance Liquid Chromatograph - Inductively Coupled Plasma Mass Spectrometer (HPLC-ICP-MS) [8,9] and the later by Atomic Absorption Spectrophotometer (AAS)[10].

4 Successful sustainable usage of agricultural groundwater

The three observation wells installed at Kamisu observation wells No.1 of the geo-pollution observation system surrounding the organic arsenic pollution area of Kamisu City, i.e. Kamisu No. 1-A well, Kamisu No. 1-B well, and Kamisu No. 1-C well. Only the Kamisu No. 1-A well with the deepest screen depth (depth: 31.30 m to 27.50 m below G.L.) is polluted by organoarsenic compounds. No organoarsenic compounds have been detected for the

Kamisu No. 1-B well, having a screen depth in the middle part of sand and gravel alternation member (depth: 19.00 m to 15.20 m below G.L.), nor for the Kamisu No. 1-C well, having a screen depth in the upper part of sand and gravel alternation member (depth: 6.00 m to 2.20 m below G.L.).

Based on the observation results of this geo-pollution observation system, the agricultural pumping well No.1 for experimental research and the observation well No. 1 for experimental research were located on a ridge between paddy rice fields approximately 130 m from the location of the Kamisu observation wells No. 1 (Fig. 3). The details of the installed wells are as follows. The two wells were separated by a horizontal distance of 3 m.

- (1) Observation well No.1 for experimental research (screen depth: 19.50 m to 17.00 m below G.L.): Placed at the depth of the sand member between the lower part of sand and gravel alternation member and the middle part of sand and gravel alternation member.
- (2) Agricultural pumping well No.1 for experimental research (screen depth: 15.00 m to 2.00 m below G.L.): Placed at a depth extending from the middle part of sand and gravel alternation member to the upper part of sand and gravel alternation member.

The screen depth of the observation well of detail (1) is more similar to the screen depth of the Kamisu No. 1-A well, for which polluted groundwater is observed, and is lower to the screen depth of the agricultural pumping well of detail (2). On the other hand, the screen depth of detail (2) extends from the

Table 1 Concentration of organoarsenic compounds and total As in ground water of each observation wells (No.1-A:lower aquifer, No.1-B:middle aquifer, No.1-C:upper aquifer) at the Kamisu observation wells No.1

| Kamisu observation wells NO.1 | 2004/7/20~21 | | | 2005/6/12~13 | | |
|-------------------------------|---------------|--------------|--------|---------------|--------------|--------|
| | HPLC • ICP-MS | | AAS | HPLC • ICP-MS | | AAS |
| | (µg/L) | | (µg/L) | (µg/L) | | (µg/L) |
| | PAA | DPAA | T-As | PAA | DPAA | T-As |
| NO.1-A | 25 | 571.5 | 460 | 27.1 | 197.8 | 210 |
| NO.1-B | Non-detected | Non-detected | 8 | Non-detected | Non-detected | 7 |
| NO.1-C | Non-detected | Non-detected | <1 | Non-detected | Non-detected | <1 |

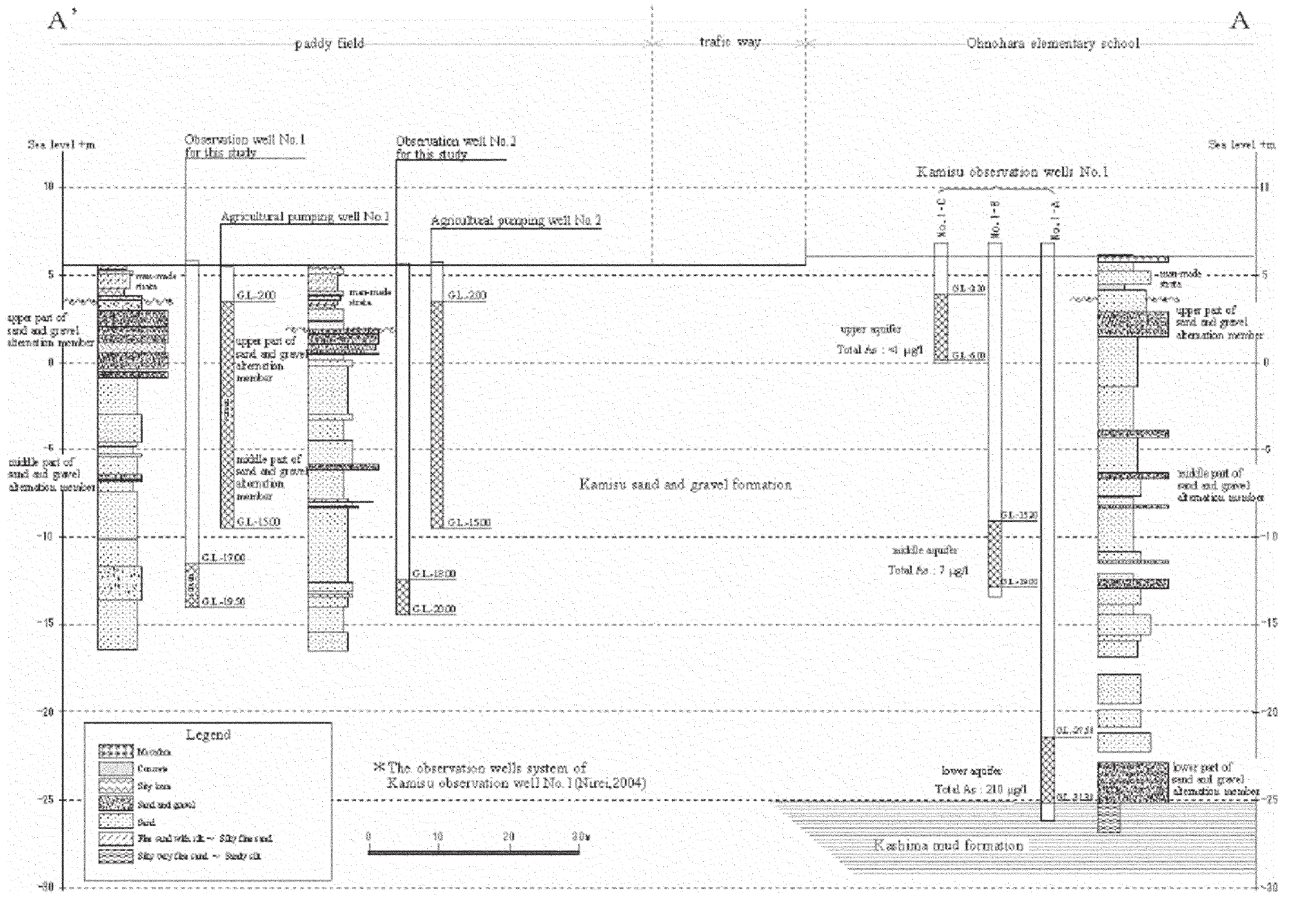


Fig.3 Geo-environmental and hydrostratigraphic cross section of A-A' and structure of each well^[7]

screen depth of the Kamisu No. 1-B well to the screen depth of the Kamisu No. 1-C well, for which no groundwater pollution has been observed.

These screen depth settings for the experimental research system are designed to determine a pumping rate for providing unpolluted groundwater. The system consists of the agricultural pumping well No.1 of detail (2), from which water is pumped; and the observation well No. 1 of detail (1), in which a polluted groundwater plume rises due to the pumping activity of detail (2) and is detected therein.

In this experimental research system, continuous pumping was performed at a rate between 180 and 200 L/min for the agricultural pumping well No. 1. The continuous pumping continued for 1600 minutes (approximately 27 hours) and resulted in a cumulatively pumped volume of 302 m³. The

maximum water level drop of the agricultural pumping well No. 1 was 2.635m, and the maximum effect on the observation well No. 1 was 0.188 m.

From the start of pumping through about the first five minutes, the water levels of both the agricultural pumping well No. 1 and the observation well No. 1 were in steady states. Regarding changes in the concentrations of total arsenic, the concentration for the agricultural pumping well No. 1 remained unchanged throughout the continuous pumping at 1 μg/L as total arsenic ^[7], while the concentration for the observation well No. 1 reached a steady state from about 800 minutes after beginning the pumping (Fig. 4).

Based on these results, rice cultivation was successful using unpolluted groundwater pumped with a roughly calculated, albeit safely conservative daily volume of approximately 150 m³ to 200 m³. However,

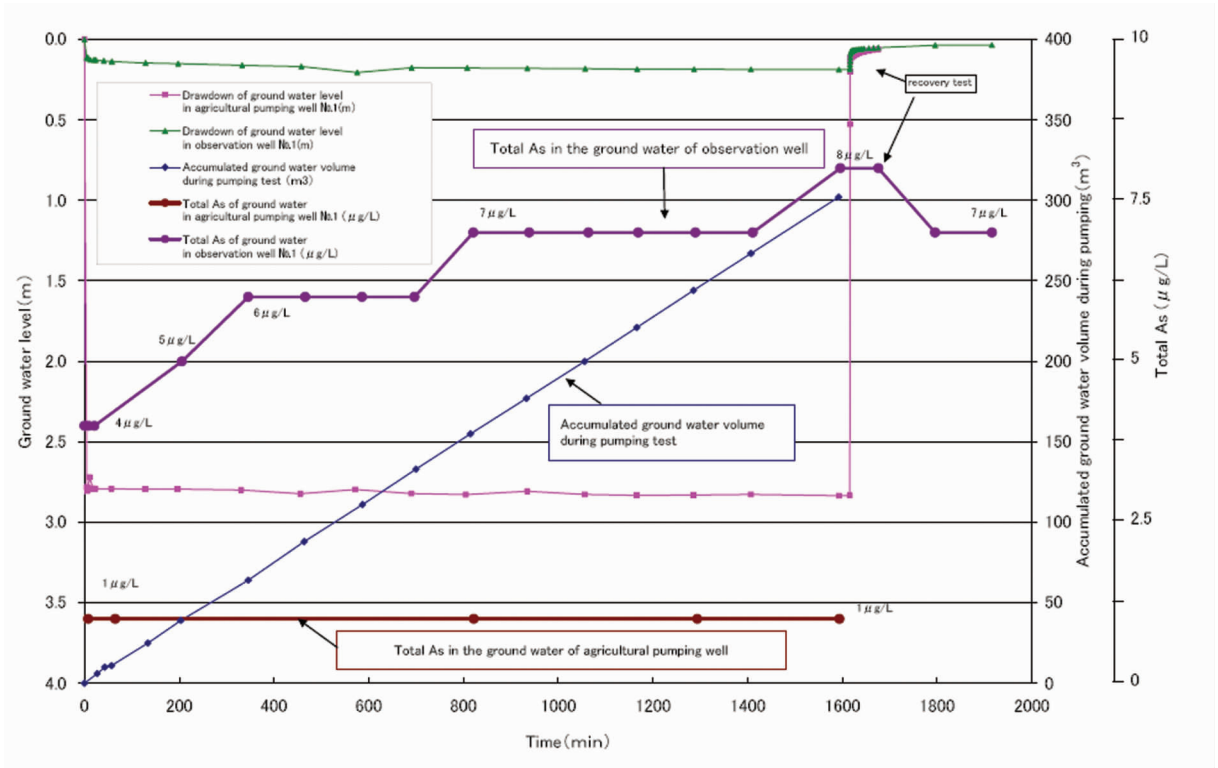


Fig.4 Results of the pumping test regarding total arsenic concentration and appropriate agricultural groundwater pumping rate^[7]

research currently continues regarding details of the appropriate pumping rate, i.e. research study on the agricultural pumping and observation wells of No.2 and the development of numerical model for the appropriate pumping rate.

5 Conclusions

The observation well for experimental research was installed with a screen placed at the depth of the sand member near the lower part of sand and gravel alternation member, and the agricultural pumping well for experimental research was installed with a screen placed at the depth extending from the middle part of sand and gravel alternation member to the upper part of sand and gravel alternation member; these wells were installed with the purpose of determining the appropriate pumping rate based on the relationship between the groundwater volume and the total arsenic concentration by observing the groundwater volume variation and the concentration change for each depth

as indices of the effects of sucking polluted groundwater upward from the lower aquifer. Additionally, based on the groundwater level variation in the observation well and the total arsenic concentration due to the pumping rate of the agricultural pumping well, it was possible to continually pump unpolluted groundwater from the agricultural pumping well.

Hitherto, much research has been performed concerning permissible pumping rates and permissible groundwater levels from economically essential conditions focused on groundwater pumping rates and land subsidence from a viewpoint of hydrogeology^[11].

Subsequently, the importance of conditions essential for life and the inseparability of these with economically essential conditions were discussed for achieving sustainability of groundwater resources^[12].

With the aim of further expanding the viewpoints recited above, and to successfully harvest unpolluted rice from paddy rice fields polluted by organoarsenic

compounds, an example of research is described here regarding a permissible pumping rate and a permissible concentration on the premise of conditions essential for life. Research concerning groundwater resources, environmental resources, conditions essential for life, and economically essential conditions thereby involves the essentials for resolving global environmental problems, and therefore is planned for more in-depth future research.

References:

- [1] Peter H. Gleick, Heather Cooley, Michael J. Cohen, et al. Meena Palaniappan. The World's Water, The Biennial Report on Freshwater Resources, 2009, 402Ps.
- [2] Selinus Olle, Alloway Brian, Centeno Jose, et al. Essentials of MEDICAL GEOLOGY. 812Ps, Elsevier, 2005.
- [3] Hisashi Nirei, Tomoyo Hiyama, Takashi Kusuda, et al. An illustrative example of the geo-pollution and the diagnostic standard for Cleanup on the geo-pollution sites -in the case of VOCs such as PCE,TCE,etc- [C]//Japan Branch of IUGS-GEM (eds.). The Proceedings of Internaonal Symosium on Geo-pollution Science, 2008:7-10.
- [4] Kazuhiro Ishii, Akira Takano, Fujio Otsuka, et al. Diphenylarsinic Acid Poisoning from Chemical Weapons in Kamisu, Japan. Annals of Neurology, Wiley-Liss, Inc., 2004, 56(5):741-745,.
- [5] Hisashi Nirei; Organic Arsenic Pollution, Geopollution and Soil Contamination in Kamisu, Japan. Sangyou to Kankyuu, 2004,377:56-62.
- [6] Hisashi, Nirei; Geopollution and Risk Management—An Example of Organic Arsenic Geopollution in Kamisu, Japan. Sangyou to Kankyuu, 2006, 406:45-48.
- [7] Tomoyo Hiyama, Hideyo Takahata, Hidefumi Ikeda, et al. How to use the groundwater resources at geo-pollution area on organoarsenic compounds[C]// Japan Branch of IUGS-GEM (eds.). The Proceedings of Internaonal Symosium on Geo-pollution Science, 2008:43-50.
- [8] Kouji Kinoshita, Mutsuo Ishizaki, Toshio Kaise. Determination of diphenylarsinic acid and phenylarsonic acid, the degradation products of organoarsenic chemical warfare agents, in well water by HPLC-ICP-MS[J]. Appl.Organometal. Chem, 2005, 19:287-293.
- [9] Ayano Noguchi; Establishment of Analysis Methods and Elucidation of the Morphisms of Environmental Phenylarsenic Compounds. Masters Thesis, Department of Life Sciences, Tokyo University of Pharmacy and Life Sciences, 2007:104.
- [10] Tomoyo Hiyama. Investigation of Groundwater Pollution by Organic Arsenic in Kamisu, Japan using Inorganic Arsenic Analysis. Masters Thesis, Graduate School of Science and Engineering, Ibaraki University. 2004:43-50.
- [11] The Research Group for Water Balance; Groundwater Resources Engineering. Kyoritsu Shuppan. 1973.
- [12] Hisashi Nirei. Environmental Geology and Environmental Education. Proceedings of the Retirement Commemoration of Professor Keiji Suzuki. Fukushima Univ., 1990:81-89.

在被旧日军毒气武器的有机砷化合物污染的日本某些地区使用地下水资源

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提要:从医学地质学角度看,在日本地质污染的地方如何使用地下水资源,我们面临许多问题。本文讨论了地质污染学(geo-pollution science)作为医学地质学中一门学科的概念以及在受二苯亚砷酸污染的地方成功使用农业地下水的案例。

关键词:地质污染;医学地质学;有机砷化合物;毒气武器;地层污染;地下水污染;地下空气污染

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