

The Current Situation of Investigations and Remediations against Oil Leakage Site in Japan.

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The Current Situation of Investigations and Remediations against Oil Leakage Site in Japan.

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Abstract In Phase 1, a site polluted with fuel oil is assessed to confirm how large the two-dimensional spread of the pollution is, and in Phase 2, the site is further closely assessed to elucidate the mechanism of pollution. The preciseness of the Phase I assessment determines whether the cleanup countermeasure will succeed or not.

In strata consisting of sand, silt, and clay layers, fuel oil more easily and more massively penetrates the sand layer because of the coarse nature of sand. Even within a sand layer, oil adhesion varies between fine sand and coarse sand.

Therefore, sand should further carefully be classified according to the particle size. We have recommended to use a gas monitor in the core analysis and analyze every 10-cm segment of the core. If the mechanism of pollution is exactly elucidated, appropriate cleanup countermeasures could be planned.

I. Introduction

At the end of March in 2002, 2,330 wells in Japan have shown pollution in excess of the environmental quality standards (according to a report from the Ministry of the Environment in December, 2002 [1]). Pollutants in excess were volatile organic compounds (VOC's) at 1,554 sites, heavy metals at 529 sites, and nitrate nitrogen and nitrite nitrogen at 865 sites (The total is more than 2,330 because there were multiple pollutants at some single sites).

Thus, geo-pollution with VOC's and heavy metals has been reported in a large number of cases. Despite this fact, pollution with benzene, the only pollutant oil regulated by the Environmental Quality Standards, has been detected only at 15 of the 1,554 sites polluted with VOC's, superficially suggesting that oil pollution was rare.

Here, we must consider the details of the pollutant classification. The Ministry of the Environment has specified 15 items of "heavy metals, etc." and 11 items of VOC's in the Environmental Quality Standards for Water Pollutants (Table 1). Among oils, only benzene is regulated as a pollutant, and toluene, xylene, etc. have been specified as substances requiring precautionary monitoring.

Business establishments dealing in benzene are regulated as the specified facility, but service stations are not regulated as such although gasoline contains benzene. This seems to explain why the reported number of oil pollution cases was so small as compared with a large number of existing gasoline stations and other potential sources of oil pollution. In light of the social situation in Japan, a large number of gasoline stations will be closed, and pollution with fuel oil will become evident in the near future in relation to post-closure land use.

We have been addressing the issue of fuel oil pollution. Because fuel oil contains benzene, toluene, ethylbenzene, xylenes, etc., we include them in the target substances to be analyzed in the oil pollution investigation. These substances are volatile, but adhere easily to analytical instruments unlike trichloroethylene or tetrachloroethylene, so that special precaution is needed in the on-site analysis. We here report our methods of investigation and cleanup countermeasures while showing some actual examples.

Table 1 Environmental Quality Standards for Water Pollutants

Heavy metal etc.		VOC's	
Substances	Standard Values	Substances	Standard Values
1 cadmium	<0.01mg/l	16 dichloromethane	<0.02mg/l
2 total cyanogen	not detectable	17 carbon tetrachloride	<0.002mg/l
3 lead	<0.01mg/l	18 1,2-dichloroethane	<0.004mg/l
4 chromium (VI)	<0.05mg/l	19 1,1-dichloroethylene	<0.02mg/l
5 arsenic	<0.01mg/l	20 cis-1,2-dichloroethylene	<0.04mg/l
6 total mercury	<0.0005mg/l	21 1,1,1-trichloroethane	<1mg/l
7 alkyl mercury	not detectable	22 1,1,2-trichloroethane	<0.006mg/l
8 PCBs	not detectable	23 trichloroethylene	<0.03mg/l
9 thiuram	<0.006mg/l	24 tetrachloroethylene	<0.01mg/l
10 simazine	<0.003mg/l	25 1,3-dichloropropene	<0.002mg/l
11 thiobencarb	<0.02mg/l	26 benzene	<0.01mg/l
12 selenium	<0.01mg/l	Precautionary monitoring Substances Guideline Values	
13 nitrate-N and nitrite-N	<10mg/l	trans-1,2-dichloroethylene	<0.04mg/l
14 fluoride	<0.8mg/l	toluene	<0.6mg/l
15 boron	<1mg/l	xylene et.all	<0.4mg/l

Environmental Quality Standards for the Human Health

II. Environmental quality standards for oil pollution

Among substances usually contained in oil products, benzene is the only substance regulated by the environmental quality standards, and therefore, determination of the benzene concentration is essential in investigating oil pollution. According to "the standards for soil pollution" and "the standards for groundwater pollution", the concentration of benzene must be 0.01

mg/l or less (If soil is the case, this standard value is applied to the test solution obtained by the specified methods of elution). Benzene is contained in various oil products, and its concentrations in gasoline are about 0.5 to 1%. Toluene and xylene in groundwater are not currently regulated by the environmental quality standards. However, they are included in the substances requiring precautionary monitoring, and their guideline values are 0.6 mg/l or less for toluene and 0.4 mg/l or less for xylene. Gasoline also contains these two substances.

Some foreign countries also regulate ethylbenzene, MTBE (methyl tertiary-butyl ether), an octane number improver, total petroleum hydrocarbons (TPH's), and polycyclic aromatic hydrocarbons (PAH's). Standard values have not yet been specified for TPH's or PAH's in Japan, but will be specified in the future as in Europe and America. TPH's in strata are determined by appropriately combining two methods of extraction (solvent shaking extraction and high temperature, high pressure solvent extraction) and two methods of assay (gas chromatography and infrared spectroscopy).

The U. S. Environmental Protection Agency (U.S.EPA) has stipulated that in quantitative estimation of TPH's, they should be separated into gasoline range organics (GRO's) corresponding to C₆ to C₁₀, and diesel range organics (DRO's) corresponding C₁₁ to C₂₈. Organics corresponding to C₂₉ to C₄₄ are usually estimated as lubricating oil range organics although EPA has not specified this class.

III. Forms of oil pollution

Oils are lighter than water and only slightly soluble in water. Accordingly, oil pollution occurs predominantly in forms of adhesion to the vadose zone and floating on the surface of groundwater. Leaked oils go down to the surface of groundwater according to the terrestrial gravitation, and spread over the water because of their low specific gravity. The body of pollutants occurs as a mass of oils concentrated in capillary zone.

Such masses are referred to as "free products". A part of the oils dissolve in groundwater, diffuse along the stream of water, and accumulate usually in a relatively shallow part of the groundwater (Fig. 1).

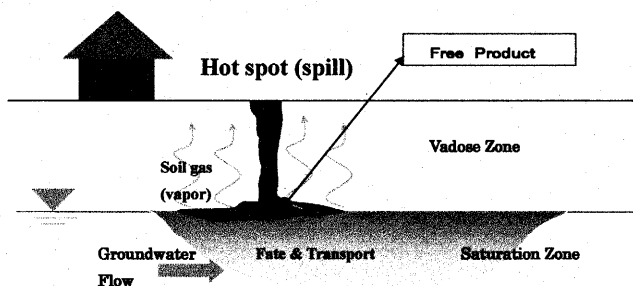


Fig. 1 Forms of oil pollution

A fact-finding investigation needs surface pollution investigation, core boring, and trial boring to confirm the existence and state of free products as well as oil penetration into strata.

IV. Oil pollution investigation

Fuel oil pollution investigations are fundamentally similar to those for VOC's.

Through the Phase 1 assessment, the following information is to be obtained:

- Site history (history of land use, history of changing underground tanks, accident history, operation procedures at the service station, etc.) and its surrounding receptors (drinking water wells, surface water, underground storage sites for goods for common profit, waste water drains, etc.)
- Layout diagrams indicating the location of underground tanks, piping, measuring instruments, oil/water separators, wells, etc.
- Evidence suggesting oil leakage (discoloration of strata, poor plant growth, leakage from containers, inventory shortage, etc.)
- Geology and hydrogeology of the site-surrounding area, and the level and flow direction of groundwater
- Gas concentrations in the detector and in the surface soil samples taken from the whole area of the site

The Phase 2 assessment three-dimensionally investigates the polluted area identified by the Phase 1 assessment, and elucidate the mechanism of pollution. When geologic stratum samples are analyzed, special attention is needed. Gasoline, kerosene, light oil, and lubricating oil are less volatile than VOC's (excluding gasoline). If once they adhere to sampling bottles or sensors, they cannot easily be washed out, and may cause estimation troubles or make the analytical instruments unusable.

Oils, especially oil products, are less dense than water, and therefore, they are likely to heavily pollute groundwater table [2]. Close observation of core samples is recommended because the presence of oil pollution of the sample can easily be confirmed visually. When the core is immersed into water, oil slick will appear if the core has been polluted with oil. This phenomenon will contribute to the assessment.

In a stratum consisting of sand, silt, and clay layers, the sand layer will be permeated with larger amounts of oil because of its coarseness. As a result, striped oil pollution is frequently observed in alternation strata consisting of sand and silt. Even within a sand layer, oil adhesion varies between fine sand and coarse sand. Therefore, sand should further be classified according to the particle size.

Volatile oils such as gasoline and light oil may

massively be retained on the surface of groundwater. Because this oil load depresses the groundwater level, it is recommended to install an observation well, measure the water level and oil thickness at the same time, and adjust the measured water level for the depression by oil load. Such adjustment is necessary when different observation wells are compared with one another.

At a site where light non aqueous phase liquids (LNAPL's) and dens non aqueous phase liquids (DNAPL's) exist in combination, they dissolve in each other, and pollution may extend to a deep layer of the stratum under the influence of DNAPL's.

Polluting oil products are differentially retained in different layers according to their geological characteristics (sand, gravel, clay, etc.). Therefore, sampling and sample analysis should carefully be carried out. The extent of oil adhesion also vary somewhat among fine, middle, and rough sand particles. A close on-site analysis is required for the oil pollution investigation (Fig. 2).

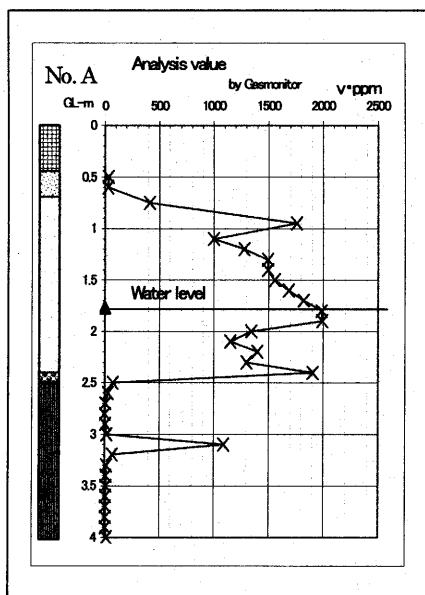


Fig.2 core analysis result example

Fig. 2 shows an example of boring core analysis conducted at a site of oil pollution. Every 10-cm segment of the core sample was analyzed by using a gas monitor. It was revealed that sand and gravel layers retained high concentrations of oils, and that the amount retained varied according to the particle size of the sand. The two highest concentrations of oil lied with the groundwater level between, illustrating a characteristic pattern of LNAPL's pollution.

According to our experience in oil pollution investigations, most of underwater heavy pollution is found 1.5 to 2.0 m below the groundwater level.

Service stations have a lot of underground tanks containing gasoline, light oil, kerosene, lubricating oil (waste oil tank), etc. Oil leakage from underground

tanks or pipes can be detected by surface pollution investigation or core boring, but the kind of oil cannot be identified by on-site GC/PID analysis.

Gas chromatography/distillation analysis or TLC-FID analysis (iatroscan analysis) is used to differentially determine what kinds of oil are responsible for, and elucidate the mechanism of oil leakage. In the case shown in Fig. 2, the pattern of oil pollution is well demonstrated, but does not give information about what oils were responsible. In such a case, it is further necessary to sample heavily polluted strata, and analyze the kind of oil involved.

At the site No. A, samples for oil analysis were taken from the depth (GL-1.8 m) at which the highest concentration of oil was detected.

Fig.3 shows the results of the oil analysis. Among TPH's, fractions of C₆ to C₁₀ and C₁₀ to C₂₈ showed high values, suggesting that gasoline, kerosene, and light oil were the responsible pollutants.

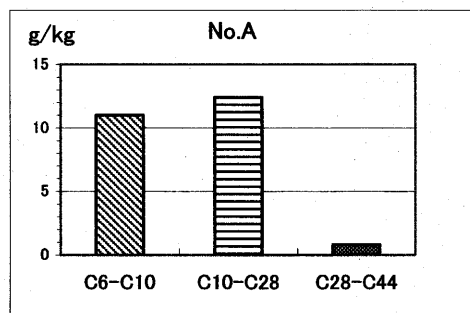


Fig.3 Result of TPH's

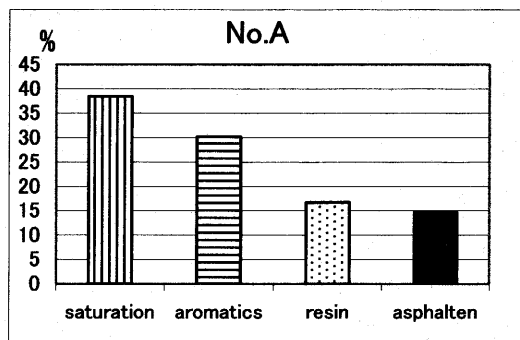


Fig.4 TLC-FID Analysis

TLC-FID analysis revealed a large amount of saturated organics and aromatic components, suggesting that gasoline and kerosene may be involved in this pollution (Fig. 4). This sample contained resins at about 15%. Usually, resins are not contained in gasoline or light oil. They were probably formed as a result of time-related deterioration of oils. Thus, it seemed that a relatively long time had passed since the underground penetration of pollutant oils occurred.

The detected asphaltene probably originated from

coal tar used as an anticorrosive for underground tanks. It seemed likely that anticorrosive coal tar was accidentally dissolved in gasoline or other oils. The positive detection of asphaltene may have suggested that gasoline tanks were somehow damaged or that kerosene was erroneously overflowed in the process of oil supply.

Fig. 5 shows the results of gas chromatograph distillation analysis conducted to closely examine the kind of oil penetrating into the stratum. The fractions distilled at 174 degrees or lower indicate gasoline as a pollutant; those distilled between 170 and 250 degrees indicate kerosene; and those distilled between 240 to 350 degrees indicate light oil. As shown in Table 2, this analysis revealed that the pollutants in the site examined were gasoline, kerosene, and light oil.

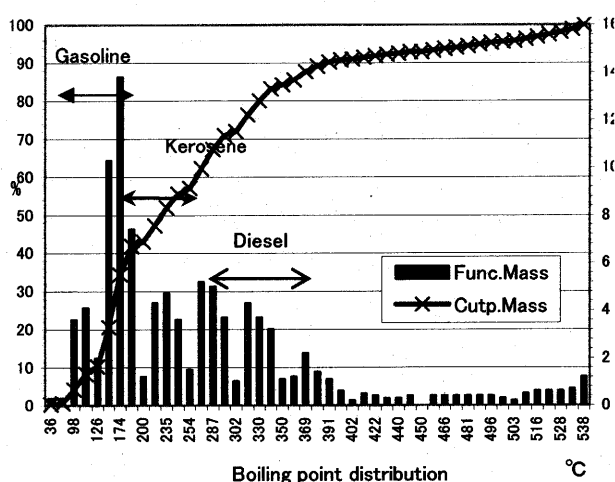


Fig.5 GC Distillation

V. Countermeasures against oils pollution

The principal point to be considered in taking countermeasures against oils pollution is the fact that the material is combustible. Actually, excavation and incineration are frequently used for cleanup.

When gasoline is massively leaked, however, these measures produce a considerable offensive odor and a large amount of volatile benzene released. Safety management for protecting occupational health damage is essential. Moreover, it is also important in designing resident safety measures and cleanup procedures to pursue prior investigations without arousing anxiety among the residents.

In oil leakage accidents, groundwater/underground air purification using double casing and ultrahigh pressure washing method were both effective in recovering soil gases and benzene that had dissolved into groundwater from the free products. In the former procedure, double casings are constructed for the well,

and soil gases and groundwater are pumped from the outer and inner casings, respectively, to recover benzene, toluene, etc [3]. In the latter procedure, air and high pressure water of 40 to 200 Mpa are jetted in combination from the drill rod to recover oils having adhered to the stratum as well as benzene, toluene, etc. having dissolved in groundwater [2]

Volatile oils can be treated similarly to VOC's, but needs special consideration. Because of their strong combustibility, pumps, blowers, and other motors must be of explosion-proof type. At a site polluted with oils, suction and activated charcoal adsorption of underground air may elevate the temperature so high that explosion may happen. Therefore, it is desired that the sucked concentrated gases (1000v·ppm or more) are treated with a combustion chamber, for example, an modified engine.

In the cleanup of a site polluted with oils, it is extremely difficult to estimate the amount of recovered oil because oils is not a single substance unlike trichloroethylene or tetrachloroethylene.

Petroleum is a general term given to combustible natural oil liquids (crude oil) and their purified products, and contains hydrocarbons (compounds of carbon and hydrogen) as main components as well as compounds of oxygen, nitrogen, sulfur, etc. as contaminants. Petroleum is separated into gasoline, kerosene, light oil, heavy oil, etc. depending on the boiling point.

The only way to estimate their amounts recovered is to convert the measured values into the amount of gasoline based on the MSDS (Material Safety Data Sheet) information given by manufacturers of petroleum.

However, even this way of estimation is not useful if considerable amounts of volatile components (benzene, toluene, xylene, etc.) have already escaped in vapor. Because these volatile components are lighter than water, most of them accumulate above the groundwater level, and therefore, a considerable amount may escape in vapor from the ground surface depending on the atmospheric pressure. Thus, the method for estimating the amount of vaporized components remains to be investigated.

VI. Conclusion

Unused grounds left after closing of service stations are now increasing. Service stations do not come under the specified facilities using toxic substances (defined in Article 2, Paragraph 2 of the Water Pollution Control Law <Law No. 138, 1970>), but oil pollution of the strata may exist. In some cases, surplus debris from excavation for use alteration of land contains mineral oil, benzene, etc. in excess of the corresponding standard values, and their acceptance may be refused by the prearranged recipient.

In other cases, benzene dissolved in groundwater may deteriorate the surrounding environment.

As a result of the growing interest in the global environment such as groundwater and geologic conservation, the soil pollution control law was put in force on February 15, 2003. Thus, the legal regulation for geologic environment has been becoming tightened now. In order to manage the environmental risk of geo-pollution, the lands of which geo-pollution is suspected should exactly be identified. Accordingly, an investigation of such lands is conducted as a matter of duty when a factory or business establishment is closed or when the purpose of its use is changed.

The enforcement of the law will increase the number of pollution investigation, but satisfactory anti-pollution measures cannot be carried out unless the behavior of toxic substances and the state of their existence are definitely confirmed. Moreover, the pollution investigation has become more sophisticated and more diversified year after year. Thus, the mechanism of pollution must precisely be elucidated, and appropriate countermeasures should be carried out according to the target of cleanup. The persons who take charge of pollution investigation should be experts who have technical backgrounds supported by much experience at many polluted sites. It seems necessary to train engineers as excellent technical experts based on a qualification system.

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