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Adsorption Properties of Sediments for Pesticides: Investigation by Supercritical Fluid Extraction and Gas Chromatography Mass Spectrometry

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1. Introduction

Use of pesticides is necessary in the recent agricultural production for removal of weeds and pests which interfere growth of crops. Though use amount and use methods are determined by standards for the each pesticide, residual pesticides in environments and foods are paid attentions much from the view point of food safety. Therefore, analytical methods to evaluate pesticide residue contained in foods are investigated well (Okihashi et al. 2005). On the other hand, pesticides spread in agricultural fields and golf links are not only taken by plants but also drawn to environment as waste water with rain water and supplied waters, and it is issued that the pesticides pass through sediments to reach to ground waters (Sudo et al., 2002). Japanese Ministry of Environment determined pesticide control law and standard indexes for golf link pesticides to monitor and control the pesticides emitted to environment (Ministry of Environment, Government of Japan, 2001). Determination methods for the pesticides contained in several kinds of samples are usually complicated and difficult to determine accurately without sophisticated skill (Ormad et al., 1996; Zhou et al., 2009). In addition, the determination methods are different with different target analyte and samples, and it takes long time to determine several kinds of pesticides. In 2005, the positive list for residual pesticides was presented and multiple analysis methods were shown such as gas chromatography (GC) analysis after supercritical fluid extraction (SFE) (Okihashi et al., 2005; Tobino et al., 2007). For each pesticide, on the other hand, liquid-liquid extraction (LLE) (Ormad et al., 1996) and solid phase extraction (SPE) (Zhou et al., 2009) are popular for the determination. However, they are time consuming and require good experimental skill and also consume much organic solvent not to be good for environmental charging. Accordingly, we tried to apply SFE method to environmental analysis which is already used for food analysis as Tobino et al. presented before (2007). The SFE is effective extraction utilizing supercritical fluid characteristics such as high permeability of the fluid and high solubility of organic solutes to the fluid. Such SFE has been applied to determination of dioxines contained in sediments (Miyawaki et al., 2003). Glazkov et al.

(1999) reported extraction of organic compounds from water samples. In that report, sample water was set in the extraction cell with glass wool. The method was very simple but water existing in the supercritical fluid behaves as catalyst to decompose the organic compounds (Janda et al., 1996). Therefore we investigated another SFE method; appropriate adsorbent was added into the sample water to collect the analyte targets and then the pesticides were extracted from the adsorbent by SFE (Chikushi et al., 2009). In this method, use of organic solvent was dramatically minimized and unstable pesticides could be measured even with SFE. In the first half of this report, we describe method development based on particle solid adsorption of pesticides in water followed by SFE and GC-MS, and in the second half we discuss pesticide adsorption properties of several sediments which were also analyzed with SFE-GC-MS.

As described in above, drawn of pesticides into environmental natural waters and sediments is a big issue worldwide. However, some of sediments might have characteristics to hold the pesticides and not to let the pesticides going downstream. Most of pesticides recently used are relatively decomposable and most of adsorbed pesticides will be gone in the sediments. Accordingly, knowledge about pesticide adsorption ability of the sediments is important to consider the moving of pesticides in the farms and golf links. Here we demonstrate the adsorption ability of sediment to the pesticides. In order to do this investigation, simple measurement method for pesticides contained in water and sediments was established. Especially water analysis is said to be difficult. We have established simple method for water pesticide analysis using SFE. Sediment pesticides were also measured by direct SFE and GC-MS analysis. We obtained useful information about adsorption properties of sediments utilizing the established methods.

2. Experimental

2.1 Chemicals

Pesticides used in this investigation was golf link pesticide mixture (26 kinds of pesticides) obtained from Kanto Kagaku. These pesticides were measurable by GC and the each standard concentration was 10 mg/L. Adsorbents tested for water extraction were following 6 kinds of adsorbents: octadecylsilane (ODS) Bondesil-C18 40 μm obtained from Varian, Tenax GR from GL Science, active carbon from Nacalai Teschue, silica gel from Nacalai Teschue, styrene-divinylbenzene copolymer XAD-4 (750 mm^2/g in dry, pore 12 nm) obtained from Sigma-Aldrich, and active alumina obtained from Nacalai Teschue. ODS and Tenax GR were washed with 5 mL of acetonitril and acetone subsequently and dried for 15 min at room temperature just before use, active carbon and silica gel were dried at 200°C for 2 h and cooled in a desiccator. The XAD was treated with acetone with ultrasonic just before use. Active carbon was used as obtained. For SFE, 99.99% carbon dioxide cylinder was used as the supercritical fluid source.

2.2 Sediment samples

We collected several kinds of sediments around Kumamoto to investigate their pesticide adsorption characteristics. They were sedimentary Sandstone, Mudstone, silty mud sampled from a Tidal flat of Ariake Sea, Japan, Kuroboku soil which was from agricultural area around Mt. Aso volcano, Japan, Akahoya ash accumulated volcanic eruptions, and Limonite which was also from Aso area but mainly composed of ferric oxide. Characteristics of these sediments were measured as follows. Sediment pH and acidic capacity were measured

with treating with 1 N KCl solution as literature by Daikuhara and Sakamoto (1911). Humus (organic matter) was determined by Tyurin's methods (Kononova, 1966). Cation exchange capacity was measured by semimicro Schollengerger method (Schollenger and Simon, 1945) with 1 M ammonium acetate at pH 7.0.

2.3 Adsorption examination of the sediments

Dried each sediment 2 g was placed in a glass column which inner diameter was 0.9 cm and the height of sediment would be 5 cm in the column. The sediments were conditioned with deionized distilled water and then 25 mL of 40 µg/L pesticide mixture was introduced into the column. After that, the column sediment was washed with 25 mL of water and all eluent was collected to 100-mL conical flask. The sediments were taken from the column and dried in a desiccator overnight to be ready for SFE. The eluted waters were treated with XAD resin as described before (Chikushi et al., 2009). Namely 2 g of washed XAD was added to the water and stirred for 15 min. Then all resins were collected on a filter and dried overnight.

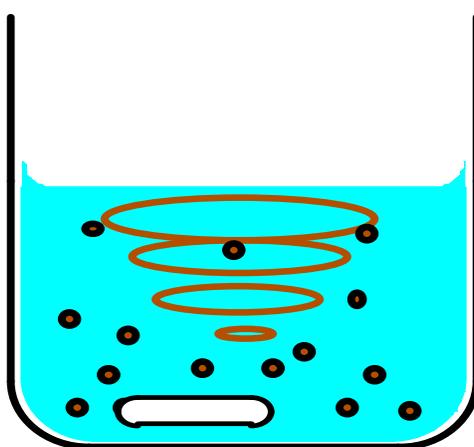


Fig. 1. Adsorption of aqueous pesticides onto the solid particle adsorbents. Appropriate adsorbent was added into 50-mL water sample and stirred for 15 or 30 min in a 100-mL beaker.

2.4 SFE extraction of pesticides from water and sediment samples

The XAD all resins after water extraction or the sediment all sample treated with the pesticides were taken in each small beaker (50 mL) and mixed with 2.0 g of wet support (diatomite) well. The mixed sample was placed in a SFE cartridge and acetone or methanol was added as a modifier. The cartridge was set in a SFE instrument, model SE-30 purchased from Isco. Typical SFE condition was temperature 50°C, pressure 3000 psi, residence time 15 min, flow time 15 min and restrictor temperature was set at 60°C. The outgoing vapor from the SFE was captured with 5 mL of acetone which was concentrated with nitrogen flow to be 1 mL afterward. The extracts were analyzed by gas chromatography-mass spectrometry (GC-MS) utilizing 6890N/5973 from Agilent or GC ultra DSQ from Thermo Electron. Injected sample volume was 2 µL in splitless mode and carrier gas was helium flowing at 1 mL/min. Separation column used was InertCap 5MS/sil which was 0.25 mm in inner diameter, 30 m in length and 0.25 µm in the film thickness. Oven

temperature was initially 50°C for 2 min, ramped to be 120°C at the rate of 20°C/min and upto 270°C at 5°C/min. The each pesticide was analyzed at the indicated M/z number in single ion monitoring (SIM) mode.



Fig. 2. Supercritical fluid extraction instrument used in this investigation

3. Results and discussion

3.1 Water analysis with SFE

Firstly we investigated how to analyze pesticides contained in water. This is important because conventional water analysis is complicated. We use SFE for sediment analysis, so if the same SFE method can be applied to water analysis, a series of measurement would be quite convenient. Therefore, our strategy for water pesticide analysis was adsorption of solid adsorbent and extraction from adsorbent by SFE. This running cost is much cheaper than solid phase extraction using commercial cartridges and not affected by extraction condition such as sample flow rate. There is no need of solvent exchange of sample in the pretreatment which is necessary in conventional solid phase extraction with cartridges.

Adsorption properties of the each adsorbent were tested and the results obtained by 15 min adsorption were plotted against octanol/water partition coefficient ($\log K_{ow}$). Interestingly, most of the adsorbents showed relationship between the adsorption property (recovery of pesticide) and $\log K_w$ in this condition, especially in cases of XAD and silica gel. On the other hand small relationship was observed in cases of ODS and Tenax GR. With these adsorbents, recoveries of the pesticides were mostly quantitative and it can be said that the pesticide molecular sizes were suitable for the adsorption on those. These results agreed

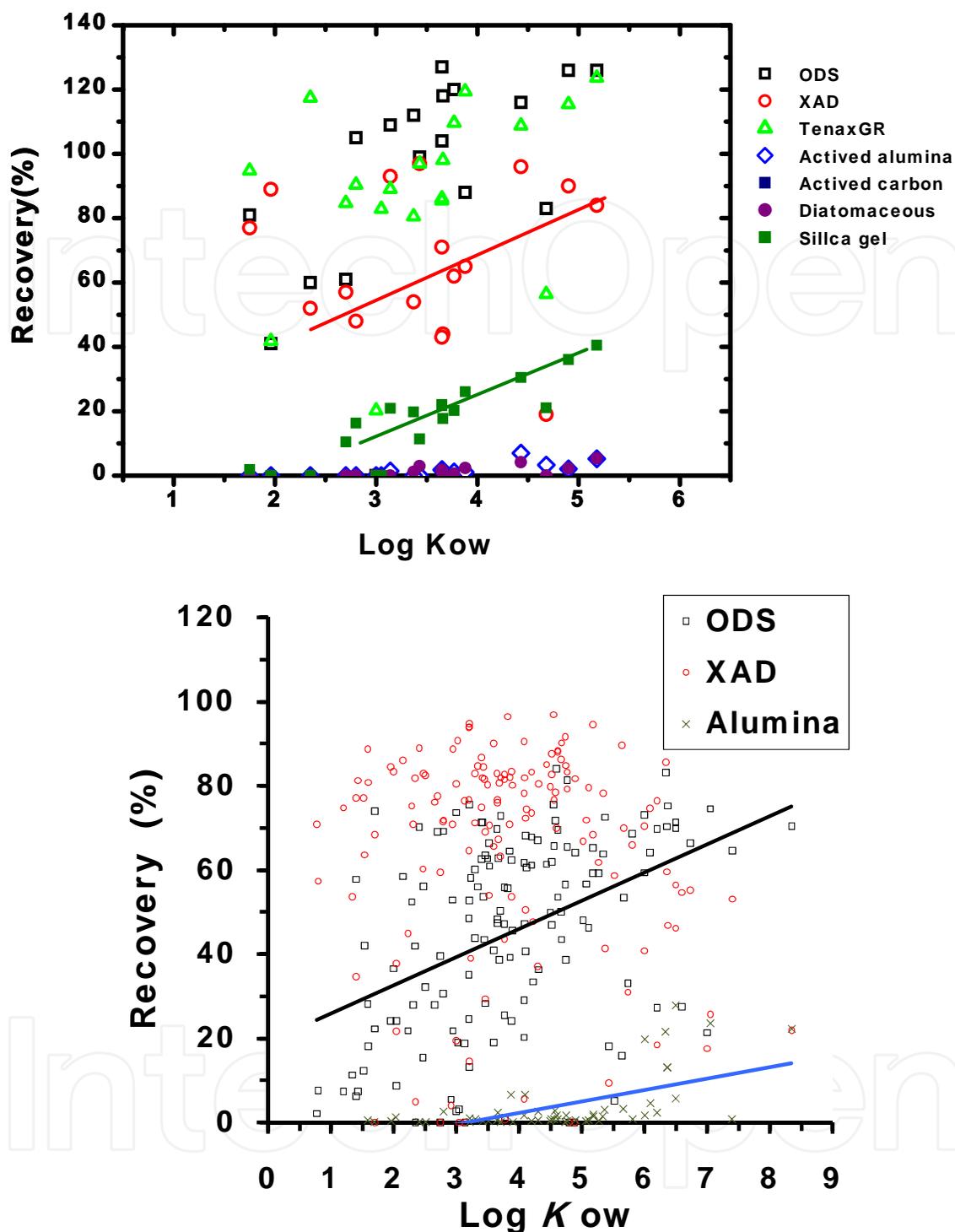


Fig. 3. Recoveries of pesticides obtained in the 15-min adsorption of 20 µg/L pesticide test plotted against their octanol/water partition coefficient (top) and same examination for 100 µg/L of 170 kinds of pesticides examined with XAD, ODS and alumina (bottom)

with the reported results by Junk and Richard (1988) where they evaluated for ODS. From the data shown in Fig. 3 and other data, it was decided that ODS, XAD and Tenax GR were suitable for the pesticide adsorption. However, Tenax GR was not used in the further experiments due to high cost of the adsorbent.

Next, effect of adsorption time was tested. Adsorption time where the adsorbent in sample water was stirred was changed 5, 10, 15, 30 and 60 min and recoveries were plotted against the adsorption time. In case of ODS, the amount was saturated at 15 min and did not increase in the longer adsorption. Meanwhile, adsorption equilibrium was completed at 30 min in case of XAD. It seemed that adsorption onto ODS occur only on the adsorbent surface while pesticide molecules enter inside of XAD particles. That is why equilibrium times were different with these adsorbents. Average particle sizes were ODS 0.04 mm and XAD 0.6 mm. It means that relative surface area to their weight for ODS was 15 times greater than that of XAD. This was also the reason of fast equilibrium in case of ODS. According to these results, adsorption times were decided as 15 min for ODS and 30 min for XAD.

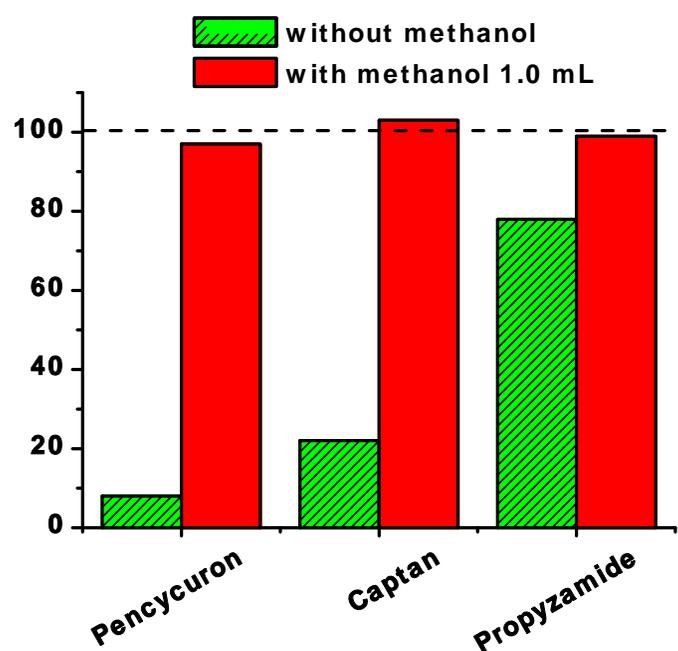


Fig. 4. Effect of methanol as modifier. Methanol 1 mL was added in the SFE cartridge as modifier. Recoveries for pencycuron, captan and propyzamide obtained with and without methanol were shown. SFE was performed at 50°C and 3000 psi.

After adsorption, the adsorbent particles were collected, dried overnight and then the pesticides were extracted from the adsorbent by SFE. Conditions of SFE were examined such as extraction temperature and extraction pressure. Also effect of modifier was tested. Modifier was necessary to extract effectively from the adsorbent. As shown in Fig. 4, good recoveries were obtained with methanol addition as modifier.

Effects of SFE pressure and temperature were also examined. In case of ODS, the results were mostly independent on the conditions and good recoveries were obtained from 1000 to 3000 psi; a little drop in recovery was observed at 4000 psi. On the other hand, effect of pressure was critical in case of XAD. Probably supercritical fluid must enter into the inside of XAD particle and more pressure was required in case of XAD. But good recoveries were obtained at 3000 psi or more. We decided to use 3000 psi for the both adsorbents. Effect of extraction temperature was not big as shown in Fig. 5. But recoveries and deviation were the best at 50°C. In conclusion, SFE procedure was the best at 50°C, 3000 psi with methanol as modifier.

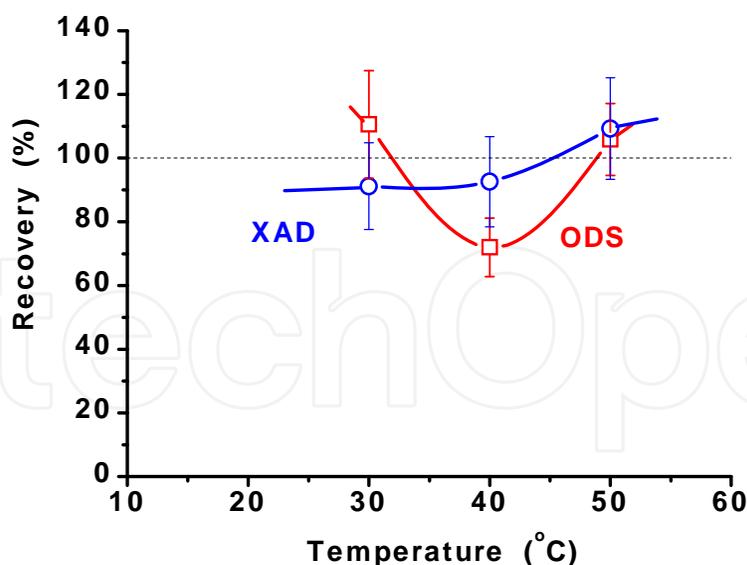


Fig. 5. Effect of SFE temperature. Methanol 1 mL was added in the SFE cartridge. SFE was carried out at 3000 psi.

The optimal conditions were obtained and recoveries of the 26 kinds of pesticides were determined accordingly for pure water as shown in Fig. 6. Peak was not obtained for isoprodion and bensride in GC-MS chromatogram due to difficulty of GC measurement. For most of other compounds, recoveries were between 80 and 120% which was said as quantitative range. Even tested concentrations were low (20 $\mu\text{g/L}$), good recoveries were obtained in this method. Mostly guideline level for the pesticide varies 30 to 800 g/L. In addition, it can be seen that recoveries with this method were obviously better than those obtained with SPE. The proposed method is simple and easy to operate and good recoveries can be obtained.

Next, linearity of calibration curve and limit of detections in this method were examined. Calibration curves for 0, 1, 5, 10, 20, 40 (or 50), 100 $\mu\text{g/L}$ of pesticides were evaluated for XAD and ODS adsorbents. Series of adsorption - SFE - GC-MS were repeated three times for each solution. For most of pesticides, good linearity was obtained (R^2 0.869 ~ 0.999 with XAD adsorption, R^2 0.963 ~ 0.9989 with ODS adsorption).

Further applications were examined; namely tea bag extraction. In this proposal, XAD was placed in a thin paper bag which was used for tea serving. The tea bag containing XAD resins was placed in a stirred water sample, and then the XAD resins were treated as same as mentioned before. Good results were obtained as well as the batch-wise collection as the chromatogram in Fig. 7. The XAD particles were relatively large and could be kept in the tea bag whereas ODS came out to the solutions in the adsorbing process. This method is applicable to on site adsorption. The tea bag containing XAD resins can be placed in stream of river water or waste water for a day or a week and taken back to the laboratory to determine. This method is expected to be useful for simple water screenings after supplying the pesticides to golf links and agricultural fields (Chikushi et al., 2009).

3.2 Sediment analysis with SFE

The five kinds of sediments obtained mainly around Kumamoto were separately placed in individual glass column after appropriate pretreatment as mentioned in experimental. Into these sediment columns, 25 mL of 40 $\mu\text{g/L}$ pesticide aqueous solution was added and gradually passed through the sediment by gravity. After all pesticide water passed the

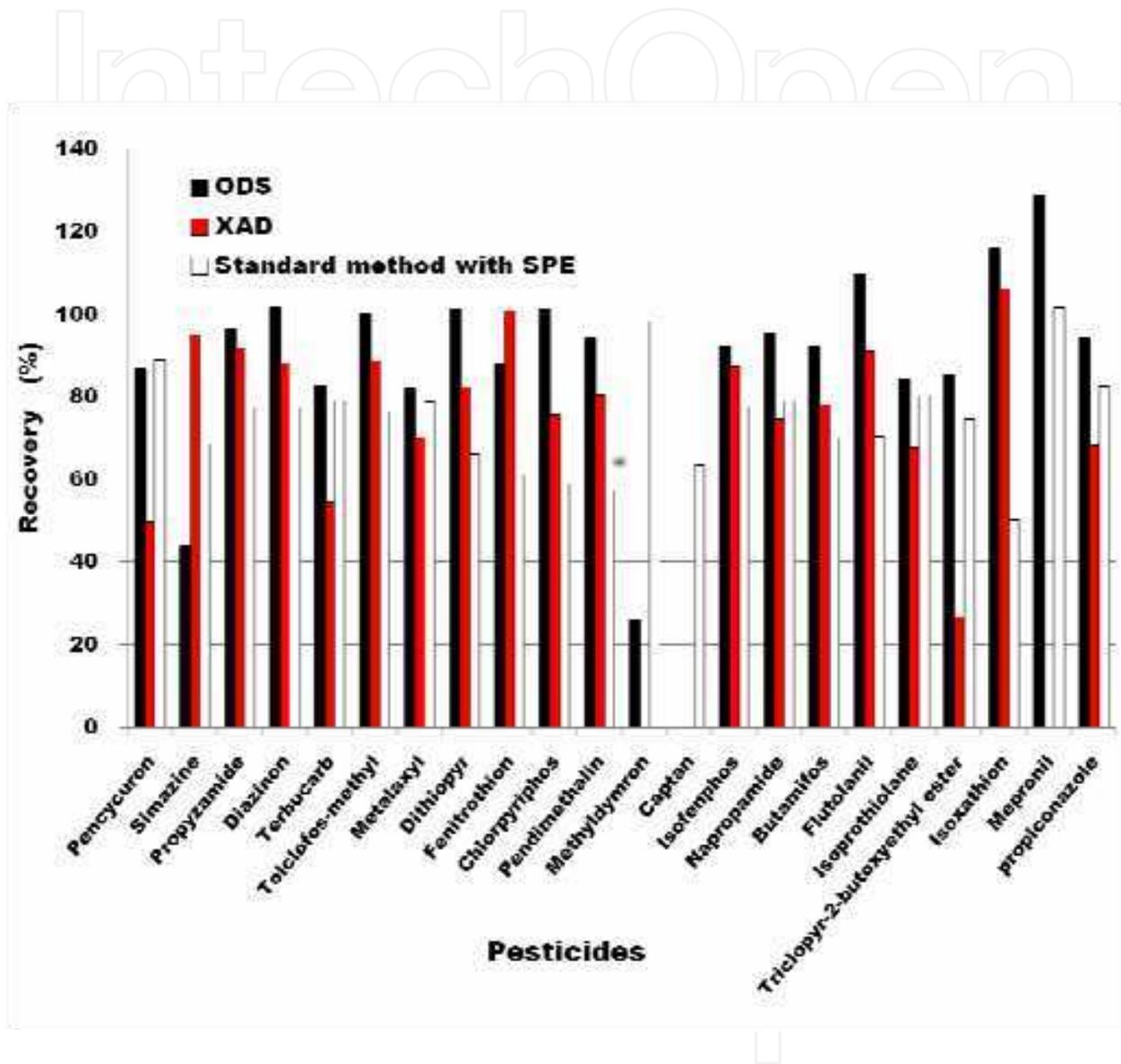


Fig. 6. Recoveries for water pesticides obtained by this method with XAD and ODS adsorbents and standard method with SPE extraction. Pure waters (50 mL) were spiked to contain 20 $\mu\text{g}/\text{L}$ of each pesticide.

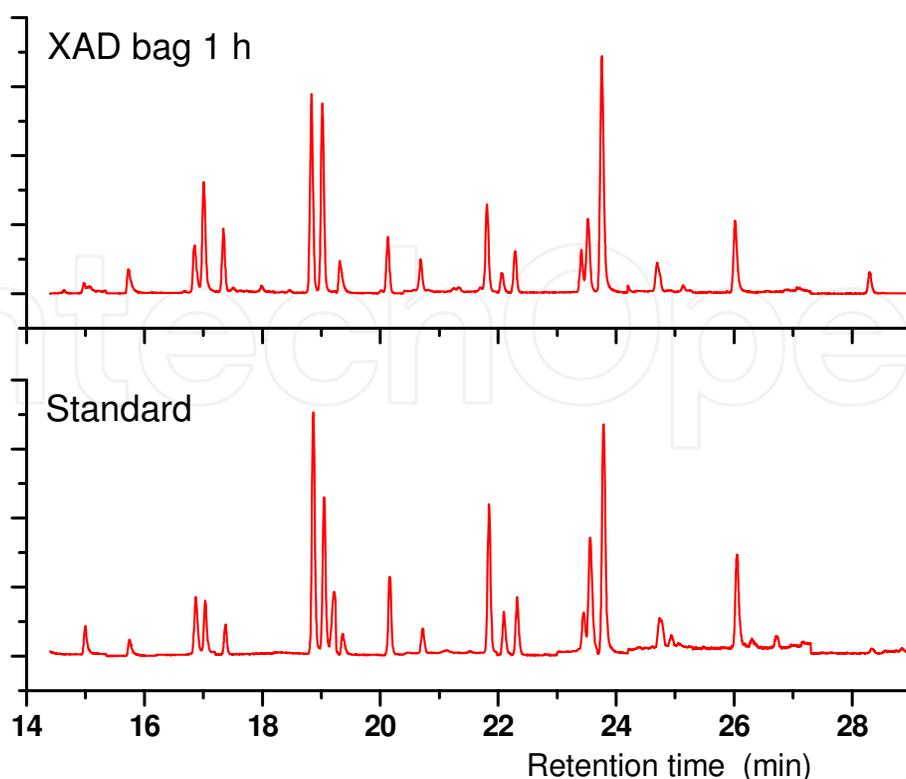


Fig. 7. GC-MS chromatograms obtained with bag sampling. The top panel chromatogram was obtained by bag sampling where XAD resin was placed in a tea bag and put in 50 mL of 20 $\mu\text{g}/\text{L}$ aqueous sample water. The bottom is for comparison: 1-mg/L standard (acetone medium) was injected directly without any treatment.

sediment, pure water 25 mL was flowed through the column. All eluents were collected under the column. Pesticides adsorbed in sediments and eluted waters were measured with direct SFE and XAD adsorption and SFE as described before, respectively. Adsorption efficiencies were obtained from the pesticide amounts remaining in sediments and eluted with water and calculated results are shown in Table 1.

As shown in Table 1, good adsorptions were observed with Ariake Sea tidal flat sediment, kuroboku soil, limonite and mudstone in this order. The pesticides were not trapped in akahoya ash and sandstone.

3.3 Properties of sediment and pesticide adsorption

First, sediment determination method with SFE-GC-MS was evaluated. 1 mL of 1-mg/L pesticide mixture was added to sediment, stored in desiccator overnight and the pesticides were extracted with SFE to measure by GC-MS. Results are shown in Fig. 8. For most of pesticides, reasonable values (100 \pm 20%) were obtained with this method.

Generally, adsorptions of non-ionic hydrophobic compounds such as these pesticides are related to organic matter contents of sediments. Characteristics of sediment vary in dependent with place, depth, surrounding conditions. Physical and chemical properties of sediments were investigated to make clear the relationship between the sediment characteristics and adsorption property.

Organic contents (humus) was extremely high in Kuroboku soil (25.1%) compared with the other's (0.45 ~ 2.84%). Organic contents are thought to help adsorption of pesticides with

	Kuro- boku	Aka- hoya	Mud- stone	Sand- stone	Tidal	Limo- nite
Pencycuron	85	1	62	6	90	82
Simazine	3	0	1	5	7	64
Propyzamide	22	0	3	1	8	5
Diazinon	41	0	8	2	32	98
Terbucarb	25	0	5	1	13	40
Tolclofosmethyl	99	3	45	5	99	82
Metalaxyl	8	4	13	10	9	41
Dithiopyr	99	3	39	2	97	90
Fenitrothion	81	0	17	0	81	67
Chlorpyrifos	97	6	76	7	97	96
Pendimethalin	80	14	83	6	82	97
Methyldymron	7	0	2	0	4	27
Captan	17	10	9	22	31	7
Isofenphos	66	1	11	1	47	61
Napropamide	50	0	14	1	57	81
Butamifos	98	2	34	1	95	82
Flutolanil	51	1	11	0	27	27
Isoprothiolane	41	0	8	0	30	58
Trichlopyrbutoxyethyl	96	3	83	6	95	96
Isoxathion	91	9	53	5	51	35
Mepronil	64	1	16	0	47	40
Propiconazole	48	0	0	0	76	100
Pyridaphenthion	42	45	68	67	48	52

Table 1. Relative amount of pesticides absorbed onto the 6 kinds of sediments in %

	Exchange acidity	pH (KCl)	Humus content, %	Superficial area, m ² /g	Cation exchange capacity, mmol/kg
Sandstone	0.97	6.12	0.45	1.01	36
Mudstone	1.41	7.07	0.64		41
Limonite	40.5	3.44	1.53	86.3	145
Akahoya ash	2.88	5.76	2.23	105	24
Tidal flat sed.	2.86	4.98	2.84	28.0	155
Kuroboku soil	23.3	4.47	25.1	38.1	373

Table 2. Properties of sediments tested for pesticide adsorption

hydrophobic interaction. Also, humus contains carboxyl groups and phenol OH and they make cation exchange capacity high. Actually cation exchange capacity of Kuroboku soil was highest. These properties are thought to be effective to adsorption of relatively polar pesticides, such as fenitrothion and isofenphos etc.

Relationship between adsorption and octanol/water partition coefficient was examined. The relationships are plotted in Fig. 8. From these results, it can be said that there were clear relationships between the pesticide adsorptions and K_{ow} in adsorption onto some sediments,

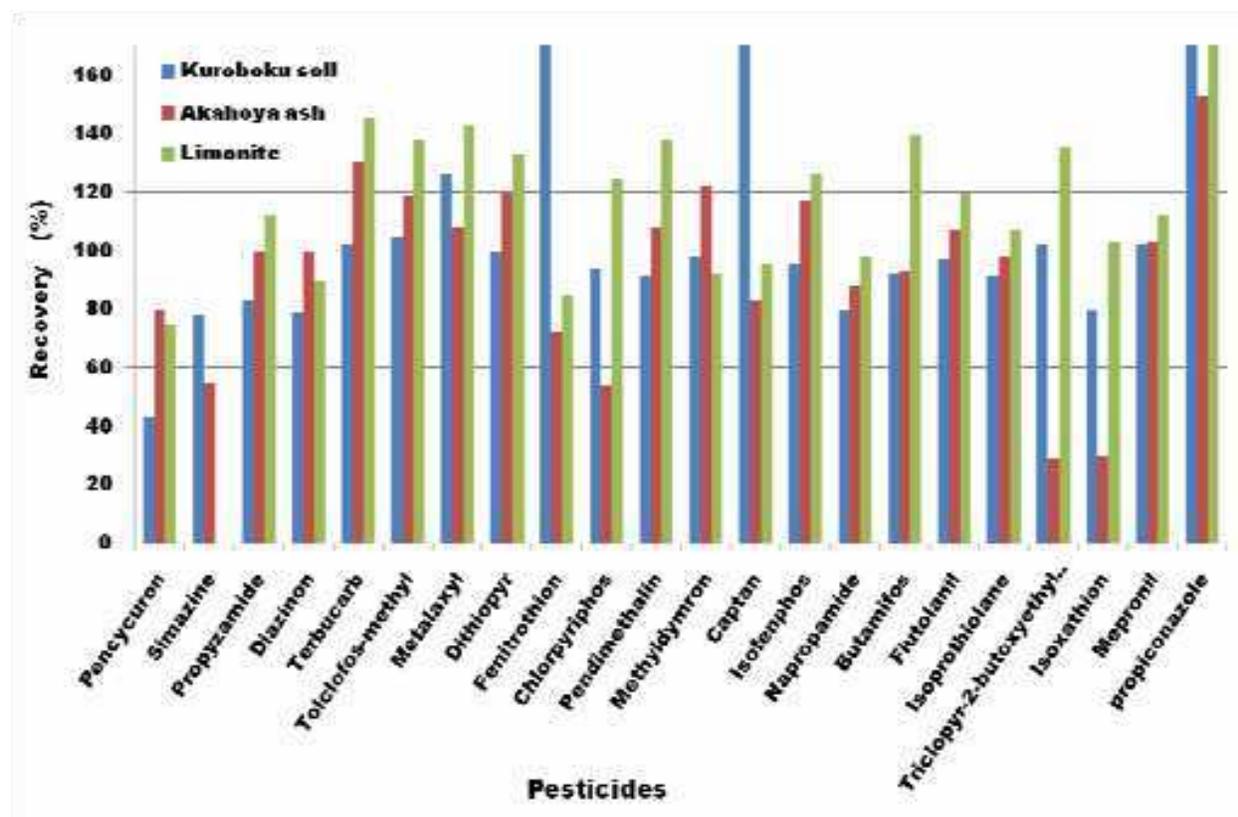


Fig. 8. Recoveries of pesticides tested for Kuroboku soil, Akahoya ash and Limonite.

especially in case of Kuroboku soil which showed highest adsorptions. The ratio of adsorption increased with increase in K_{ow} of pesticide. Similar behaviour can be seen also in Ariake Sea Tidal flat sediment. Limonite showed good adsorption property as well as Kuroboku and Tidal flat sediment but relationship with K_{ow} was worse compared to those sediments. Kuroboku and Tidal flat sediment contained organic matter much and pesticides adsorbed onto the organic with hydrophobic interaction. Also carboxyl groups and hydroxyl groups helped adsorptions in case of kuroboku and tidal sediments. Main adsorption mechanism on Limonite might be different from Kuroboku and tidal sediments. One of the factors of sediment adsorption is physical adsorption. Pesticide adsorption onto the sediments is relied on how much surface is on the sediment. For the physical investigation, superficial areas of sediments were measured and surfaces were observed with scanning electron microscopy (SEM). The Akahoya and Limonite had large superficial area ($\sim 100 \text{ m}^2/\text{g}$). These sediments showed good efficiency for the adsorption but lower than Kuroboku and tidal sediment. It can be said that surface area is important factor but content of organic matter is more critical for the pesticide adsorption. Sandstone and mudstone, which had small surface area and small organic content, did show only poor ability of adsorption. In comparison of Akahoya and Limonite, Limonite was much better adsorber compared to Akahoya though both they had good surface area and poor organic matter. Main difference between them was in cation exchange capacity; Limonite ($145 \text{ mmol}/\text{kg}$) had much higher than Akahoya ($24 \text{ mmol}/\text{kg}$). It is not sure at this time but wetting property was good due to the cation exchange groups and water liquid went in the pore of the sediment microstructure well.

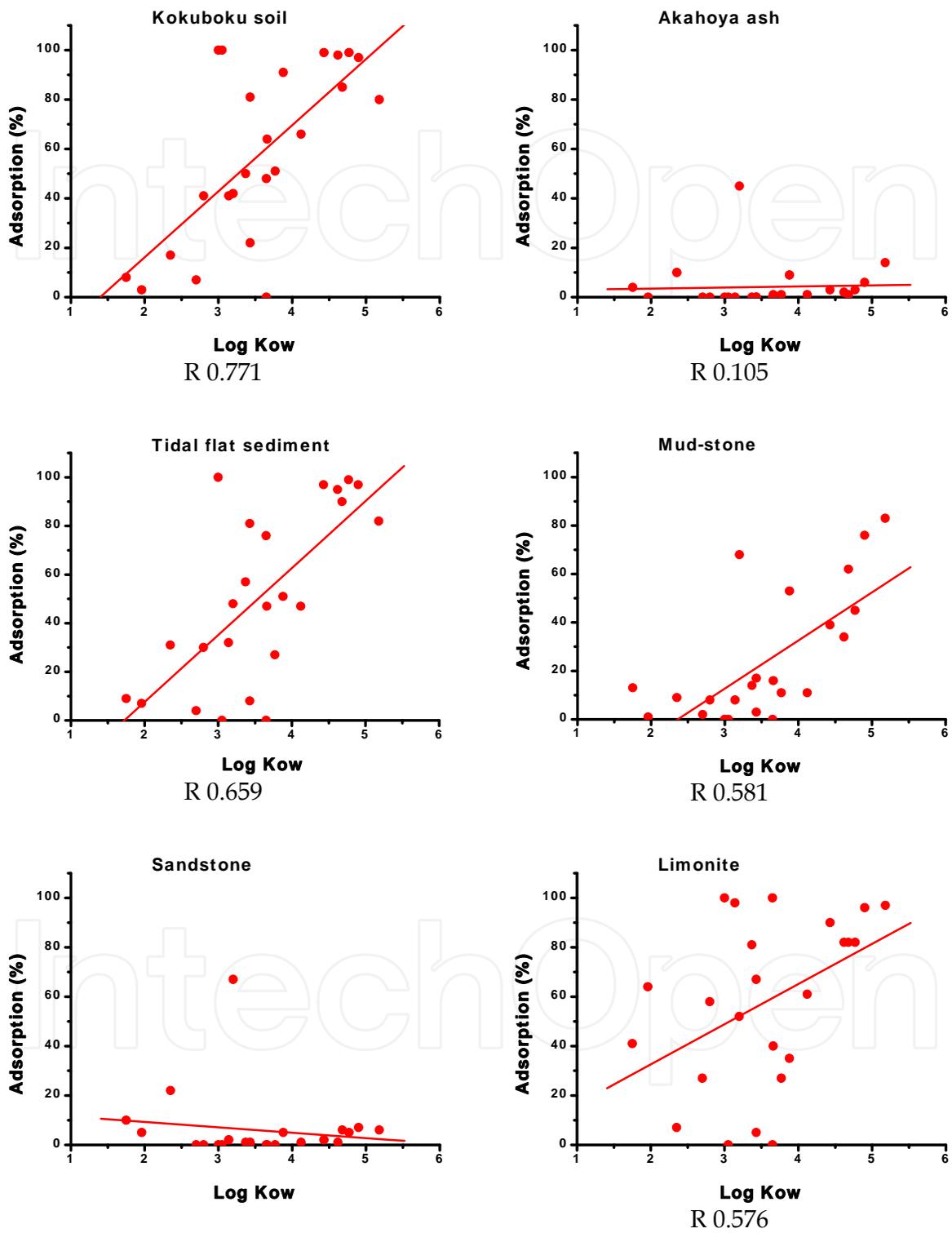


Fig. 9. Adsorption of pesticides against octanol/water partition coefficient

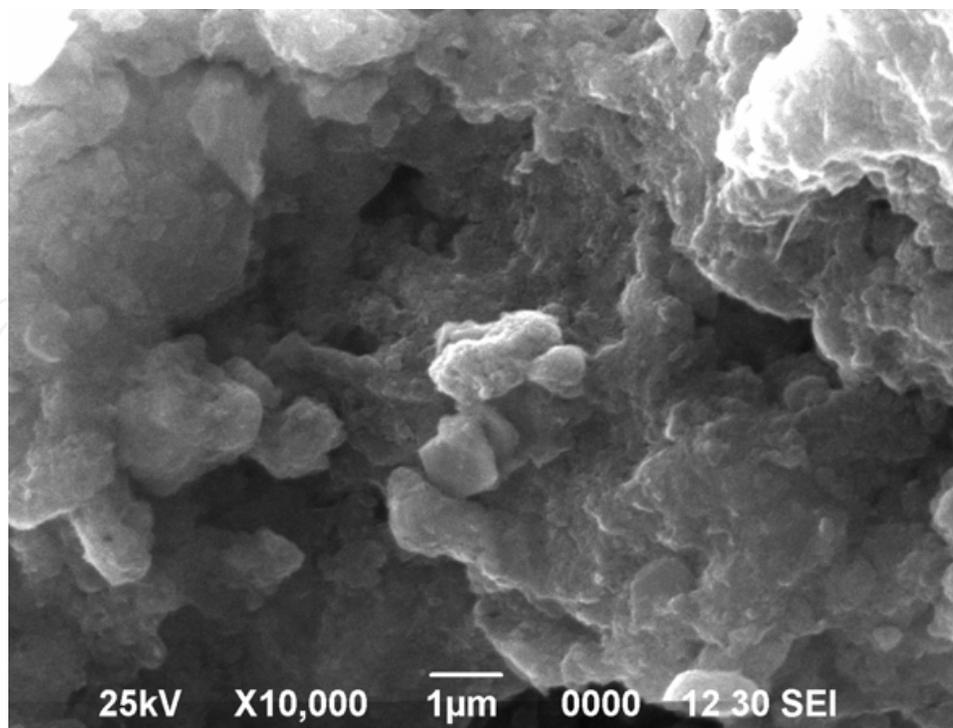


Fig. 10. SEM image of limonite observed at amplitude of x 10,000

Adsorptions are plotted against pesticide solubility to water as shown in Fig. 11. Adsorption decreased with increase in water solubility in cases of Kuroboku, Mudstone and Tidal sediments. This indicates that adsorption mechanism was same in those sediments. On the other hand, adsorptions of pesticides on Limonite were independent on the solubility. Limonite had unique adsorption characteristics for organic compounds. Kah and Brown (2007) reported that adsorption of pesticides, especially which had ionic property, was dependent of sediment pH. Pateiro-Moure et al. (2009) reported that pesticides adsorption was related with organic matter and ferric oxide. It is said that adsorption ability is not dependent of only humus in the both reports. Among the sediments tested in this work, Limonite adsorbed the pesticides well even though it had only little humus.

4. Conclusions

We have developed a simple analytical method for pesticides contained water samples by stirring of adsorbent particles in a small beaker followed by supercritical fluid extraction and gas chromatography mass spectrometry. This method provides not only labour less procedure for the measurement but also use of less organic solvent for green analysis. This is suited for screening of samples. The supercritical fluid extraction was also applied to analysis of adsorbed pesticides in several kinds of sediments. By combining water and sediment analysis both with SFE, adsorption properties of sediments were successfully investigated. More hydrophobic (large K_{ow}) pesticides adsorb more strongly to the sediments. Humus is important factor in the pesticide adsorption. Kuroboku and Tidal sediment contain high humus and adsorb pesticides well. However, Limonite which contains less humus adsorbs pesticides in good efficiency as well. This is unique property of Limonite probably due to microporous ferric oxide as a good adsorber.

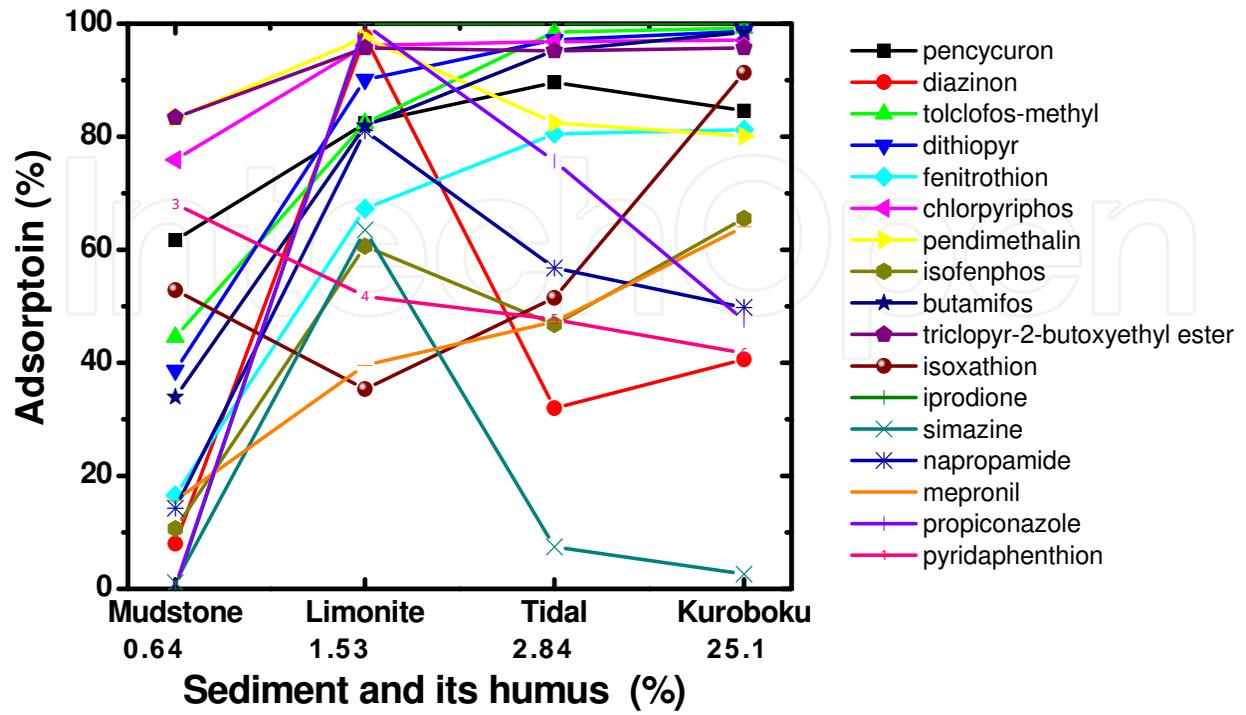


Fig. 11. Adsorption property of sediments (difference with sediment humus)

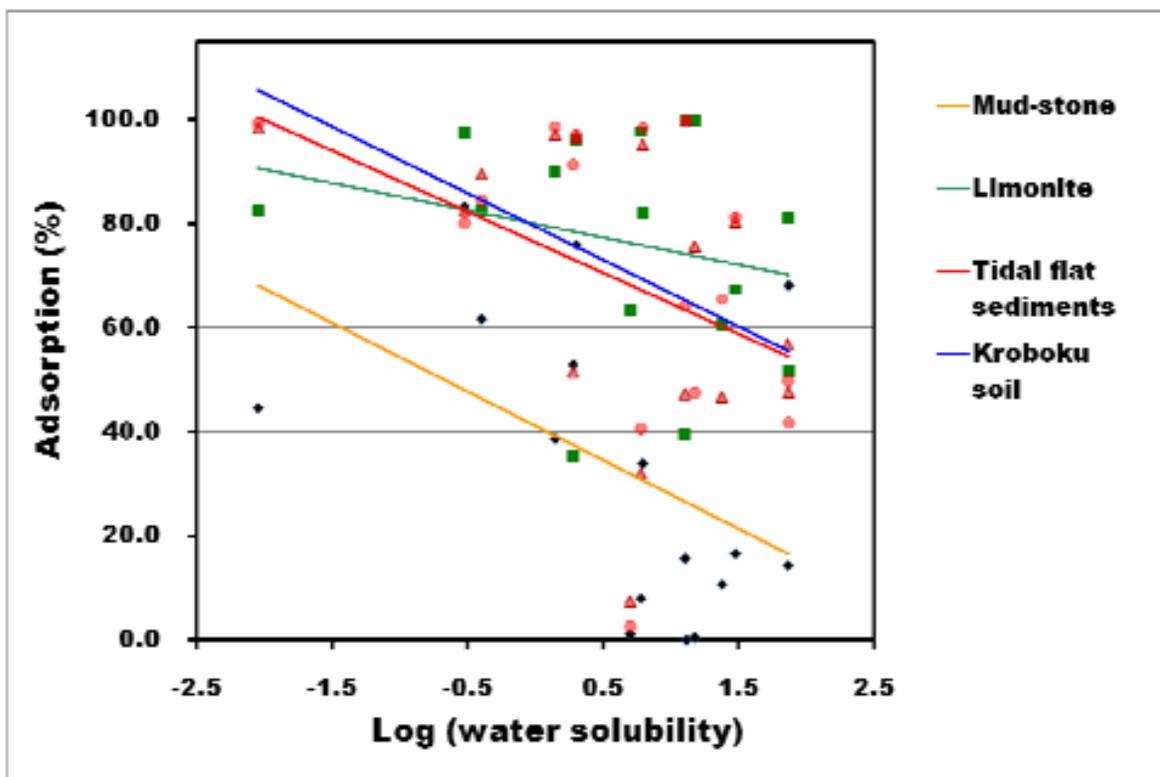


Fig. 12. Adsorption properties of pesticides plotted against their water solubility

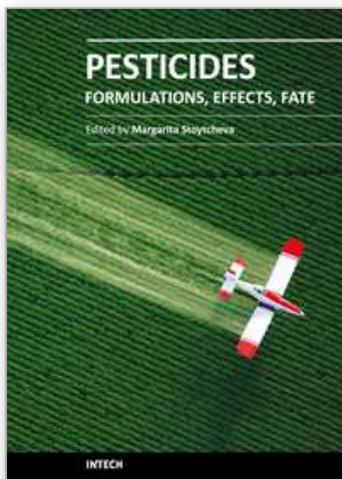
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Pesticides - Formulations, Effects, Fate

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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